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Foam Separation of Acid Mine Drainage



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Foam Separation of Acid Mine Drainage

by

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for the

Environmental Protection Agency

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Abstracts

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ABSTRACT

Laboratory studies of continuous flow foam separation were conducted to determine the optimum operating conditions for maximum extraction of dissolved metal cations (Fe, Ca, Mg, Mn and Al) from acid mine drainage. Foaming experiments were conducted in a 6 in.-diameter glass column capable of liquid flow rates of 3-12 gal. per hour. The approach to foam separation taken was the production of persistent foams which allowed protracted foam drainage to reduce liquid carry-over in the foam. The effects of pH, chelate addition, surfactant type and concentration, air sparging rate, metal concentration and foam drainage were investigated in relation to metal extraction.

The average extraction rate obtained was 1.9×10^{-7} moles total metal per cm^2 column cross-section area per minute which is approximately 4.0×10^{-7} equivalents per cm^2 per minute. Operation in simple and countercurrent foaming modes produced similar extraction rates for acid mine drainage.

The low extraction capacity of foam fractionation renders the process economically unfeasible for the treatment of acid mine drainage. The principal chemical cost is for surfactant followed by air; either alone makes the process noncompetitive.

Surfactant regeneration from collapsed foam by the addition of base was investigated as a means for surfactant reuse and cost reduction.

This report was submitted in fulfillment of Project Number 14010 FUI, Contract 14-12-876, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

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SECTION I

CONCLUSIONS

1. Continuous foam separation of mixtures of acid mine drainage (AMD) and anionic surfactants achieved the extraction of dissolved metal cations at a practical rate of 1.9×10^{-7} moles total metal per cm^2 column cross-section area per minute which is approximately 4.0×10^{-7} equivalents per cm^2 column cross-section area per minute. These rates represent 16 percent of the estimated theoretical maximum extraction capacity of foam separation.
2. Operation of foam fractionation in a persistent foam regime in order to minimize foam density requires excessive surfactant consumption which results in increased chemical costs.
3. The low extraction capacity of foam fractionation renders the process economically unfeasible for the treatment of AMD. The principal chemical cost is for surfactant followed by sparging air; either alone makes the process noncompetitive.
4. Bubble production by sparging air through porous materials, although convenient and effective, is not entirely satisfactory for control of optimum bubble diameter and a narrow bubble distribution. Bubbles tend to be larger than optimum.
5. Synthetically prepared AMD proved to be an accurate substitute for AMD in foaming tests.
6. Increasing the pH above the 2.2 - 2.3 of synthetic AMD tended to reduce metal separation, particularly for iron.
7. The use of EDTA with anionic and cationic surfactants did not improve metal separation over anionic surfactants alone.
8. Foam column operation in simple and countercurrent mode produced comparable metal removals.

SECTION II

RECOMMENDATIONS

The economic unfeasibility of foaming AMD in a persistent foam regime precludes further study of that system. The high chemical costs for foaming AMD in a persistent foam regime could be reduced by foaming in a transient foam regime which requires less surfactant. The low extraction capacity of foam fractionation, which is governed by stoichiometric adsorptive interaction of metal cation and surfactant anions, could be increased by operation in a non-stoichiometric system, such as in froth flotation, which may require less surfactant and sparging air per mass of metal removed from AMD. Further research on foam separation treatment of AMD should be directed to non-stoichiometric, transient systems.

The use of waste surfactant and air should be investigated. The combination of waste surfactant in municipal sewage, the tendency for autopurification of AMD and sewage mixtures, and the high pressure method of foam separation (bubble formation by degasification of air supersaturated liquid) appears to have favorable technical and economic feasibility and should be investigated.

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SECTION III

INTRODUCTION

Environmental degradation caused by the acidic, iron rich effluent from coal producing regions has required assiduous efforts to find cost-effective abatement and treatment methods. The treatment method for acid mine drainage (AMD) under investigation in this study is classically known as foam fractionation and often called foam separation. Separation is based on selective adsorption of dissolved surface active material (surfactant) at the liquid-gas interface of rising bubbles. Surface inactive material can be separated by coadsorption with surfactant. Separation of adsorbed and coadsorbed material from liquid is accomplished by the production and collection of foam.

The purpose of this investigation is to determine the technical and economic effectiveness of continuous-flow foam separation as a treatment method for AMD. Towards this goal, a laboratory scale, pilot plant apparatus capable of 3-12 gal. per hour was constructed and operated to define and evaluate the variables which control separation and, thus, the practical application of the method to AMD on a field scale. For expediency, the majority of work was conducted using a synthetically prepared acid mine drainage (SAMD) followed by confirming experiments using freshly sampled AMD.

Numerous small scale, laboratory investigations of foam separation, generally of a theoretical nature utilizing simplified solutions, have empirically developed the basic theory on which this practical investigation of a complex solution (AMD) is based (1-22). Even so, the complexity of a foam separation system has not permitted a single unifying theory and thus an empirical approach is necessitated. Applied investigations of foam separation for treatment of various polluting liquid wastes, a few on a pilot plant scale, have appeared (20, 23-27). Several reviews of foam separation processes are available (28-30).

This research program is divided into two main efforts; the construction phase in which the foaming apparatus was assembled and tested, and the experimental phase in which SAMD and AMD were treated. Once the apparatus was operational, the operating variables which control separation efficiency were determined within the practical limits of a potential pollution control process which in large part are restricted by hard economics.

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Foam separation is based on the phenomenon of surface activity which results from the ability of certain solutes (surfactants) to reduce the surface free energy of their solutions, and therefore the total free energy of the system, by accumulating at an interface. Surface activity as it relates to foam separation process is described using the concept of Gibbs surface excess.

$$-d\gamma = RT \sum_{i=1}^n \Gamma_i d \ln a_i \quad (1)$$

where γ = interfacial surface tension

R = gas constant

T = absolute temperature

n = number of solute components

Γ_i = surface excess of the i component

a = chemical activity of the i component

In practice foam separation consists of passing bubbles through a solution of surface active solute(s) with the aim to adsorb the solute(s) onto the gas-liquid interfaces and to remove these surfaces intact as foam, thus effecting a separation. Further, by coadsorption of non-surface active solute with surface active solutes, the former can be separated from solution with the latter. This is the case in the treatment of AMD.

An understanding of the experimental approach used here can be gained by considering three factors: (1) the particular goal of foam separation as applied to acid mine drainage, (2) the separation characteristics of the various operational modes of foam separation processes, and (3) practical consideration of the final application of this research.

Foam separation can operate in four basic modes, with each mode offering potential separation characteristics applicable to different goals (Figure 1). These goals can be described as:

1. Decontamination, in which the goal is separation of constituents from the feed to produce a purified bottom flow.
2. Recovery, in which the goal is separation and recovery in the foam of constituents in the feed.

3. Separation, in which the goal is separation of multiple constituents, one from another, by fractionation in the foam.

Obviously, the prime goal for the treatment of acid mine drainage is decontamination and, thus, the operational mode of foam separation is determined by this goal.

In comparison to simple mode operation which can be considered single theoretical plate operation, the stripper, enricher and combined modes can be considered multiple plate operations. Theoretically, the stripper mode should enhance the decontamination of the feed by providing adsorption equilibrium between bubble film and interstitial liquid of feed concentration instead of pool concentration as in the simple mode. This is accomplished by counter-current flow of feed and foam, as depicted in Figure 1. The purpose of recycling (external reflux) a portion of the collapsed foam back into the rising foam, as in the enricher and combined modes, is to further enhance the bubble film-interstitial liquid equilibrium by providing an even richer interstitial liquid than in the stripper mode. The effect of external reflux should be a higher concentration in the net overhead product, Lc-r (Figure 1) and thus a more efficient operation for recovery and concentration of feed constituents. Thus, the stripper mode should enhance decontamination of the feed, the enricher mode should enhance the recovery in the foam and the combined mode should provide the benefits of both the stripper and enricher modes.

Since the prime goal in the treatment of acid mine drainage is decontamination, the stripper mode should be given prime consideration. However, concentration of the overhead product is still desirable, not for the purpose of recovering the contaminants in acid drainage but rather for reducing the liquid volume carried over in the foam. A foam of low liquid volume is produced by drainage of the interstitial liquid out of the foam. Provision for conditions which promote foam drainage is thus required for efficient overall operation designed for the decontamination of mine drainage.

In a practical sense, the use of complex modes is often restricted by operational difficulties. For example, the distribution of liquid feed or reflux into a rising foam without causing channeling or bubble rupture is a real problem. Also, the effect of micelles introduced in concentrated reflux streams can adversely affect the bubble film-interstitial liquid equilibrium and cause a reduction of concentration in the overhead flow.

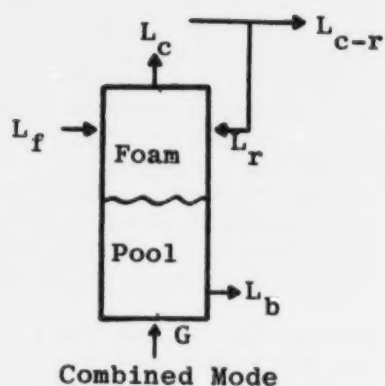
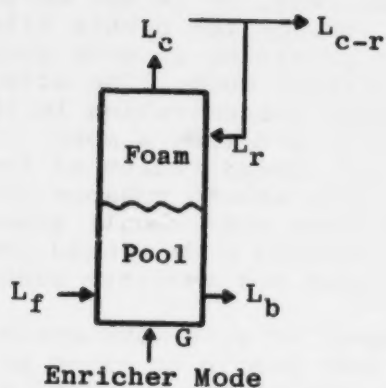
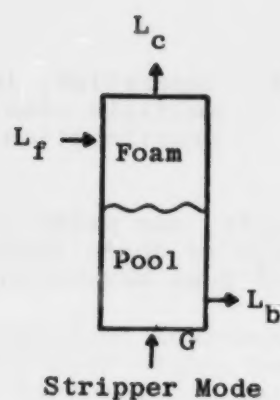
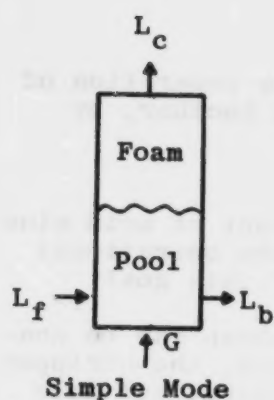


FIGURE 1

Modes of Continuous Foam Separation

L_f Liquid Feed Flow

L_b Liquid Bottom Flow

G Gas Sparging Flow

L_c Total Liquid Overhead Flow

L_{c-r} Net Liquid Overhead Flow

L_r Liquid Recycle Flow

Certain independent operating variables are known to significantly affect the separation achieved in a foam column (7) (Table 1). Not every variable is continuously variable, as bubble diameter is restricted by the flow dynamics of the system (1) and available bubble producing equipment.

TABLE 1

Independent Control Variables in
Continuous Foam Separation Processes

Geometric Variables	Solution Variables	Operation Variables
1. Bubble diameter	1. Ratio of the concentration of surfactant to contaminant.	1. Ratio of the flow rate of gas to liquid feed.
2. Column diameter	2. Chemical character of the feed.	2. Liquid feed rate as a function of column dimensions.
3. Column length	3. Specific chemical and physical interferences.	3. Foam drainage time.
		4. Modification of column to allow operation in various modes (Figure 1).

For this program, the solution variables are of secondary importance since a standard SAMD is used. The exceptions are the amount and type of surfactant required and pH effects. The main variables considered here are bubble diameter; column length, particularly as it effects liquid and foam residence times in the column; surfactant concentration or better stated for the continuous flow system the mass flow rate; gas flow rates particularly in relation to bubble diameter, solute throughput, foam density and foam stability; contaminate (metal ion) mass flow rate and operation in simple and stripper modes.

SECTION IV

FOAM SEPARATION APPARATUS

Foam Column Description - Foam separation processes are not in wide use. With the exception of particle flotation methods used in the mining industry, which are not completely analogous to foam separation of dissolved constituents in mine drainage, the state-of-the-art in foam separation knowledge and equipment is still in its infancy. As a result, not only must the physical-chemical and process engineering aspects of applying foam separation to mine drainage be studied, but, also, equipment must be designed and fabricated. The development of equipment is generally costly and time consuming, thus every effort was made to make use of commercially available equipment and/or components in order to speed fabrication.

The foam column (Figure 2) was constructed of 6 in.-ID pyrex pipe using teflon lined, stainless steel couplings at the joints. The couplings are constructed with a nearly smooth inside surface which can be significant to foam stability in the drainage sections. The foam originates at the sparging head in the lower part of the vertical section and flows up and then to the right in the horizontal drainage section. The foam passes from the drainage section down into the foam breaker (not visible) behind the control panel. Structural support for the column and auxiliary equipment is provided by an open pipe structure of dimension 15 ft. L. x 9 ft. H. x 3 ft. D. The horizontal drainage section is provided with valved ports which allow foam drainage to be removed from the column, collected in a plastic pipe which hangs below the glass pipe and either removed from the system or reintroduced at a desired point. Also, shown are liquid storage tanks, air and liquid control equipment, liquid pumps and timing devices.

The column was constructed of multiple short lengths of pipe to provide rapid manipulation of such parameters as pool depth and drainage section length which in turn control bubble residence time in the liquid and foam drainage time, respectively. Referring to Figures 2 and 3 the column has two basic configurations, the separation column and the equilibrium column. The separation column is of general design, adaptable to operation in any of the four modes (Figure 1), and was used to optimize the geometric and operating variables (Table 1) once the soluble variables were defined. The equilibrium column was designed to study the solution variables which in this case are determinations of the dynamic surface excess (an equilibrium measurement

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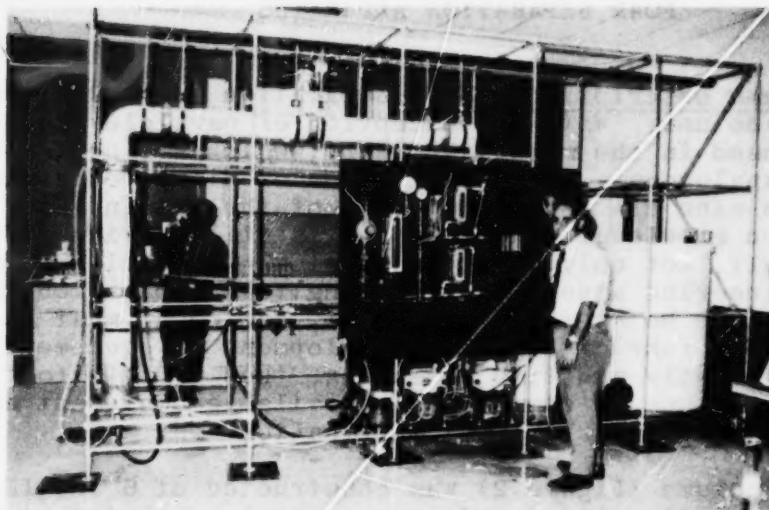


Figure 2. Separation Column. The column is shown in operation.

from which the term equilibrium column was derived) for the metallic constituents of mine drainage as a function of both various types and concentrations of surfactants in the feed. The subject of dynamic surface excess will be discussed later.

Filtered, humidified laboratory air was used for sparging. Air pressure control is provided by adjustable spring diaphragm-type regulators and gauges. Air flow was controlled with needle valves and rotameters. The various types of sparging heads tested are discussed later.

SAMD, AMD and surfactant solutions were held in polyethylene tanks. The solutions were pumped into the foaming column by positive displacement diaphragm metering pumps. The liquid flow rates are controlled by adjustment of the stroke rate and stroke length of the pumps, by needle valves and rotameters.

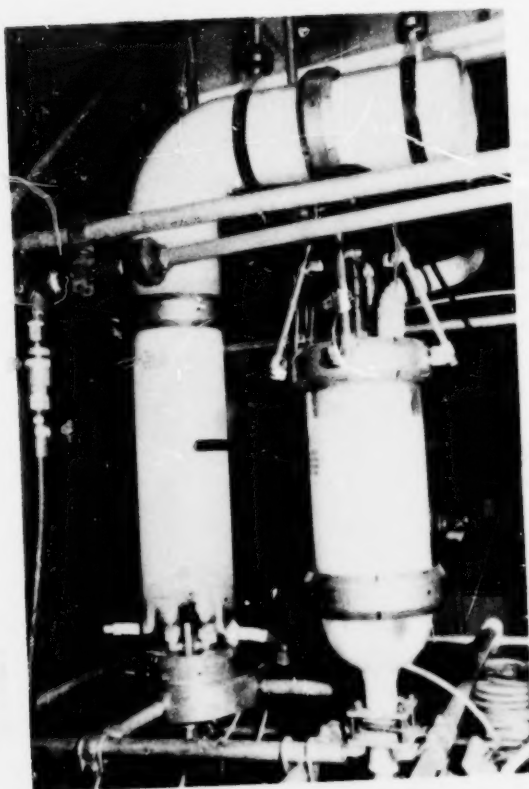


FIGURE 3. Equilibrium Column. The column is shown in operation. The absence of an extended drainage section is the only significant structural difference from the separation column. The foam breaker is shown.

Column Operation - Column operation was begun by pumping feed solution (surfactant and SAMD or AMD) into the vertical foaming section, the pool volume of which is controlled by height adjustment of the overflow discharge tube (Figure 4). The surfactant and SAMD solutions can be mixed in line or in batch prior to pumping; the later method was found more reproducible and used almost exclusively. When the predetermined static pool volume was reached, sparging was begun and the column was allowed to operate until a steady state was reached. Ostensive indications of steady state operation were stability in the height of the dynamic flooding

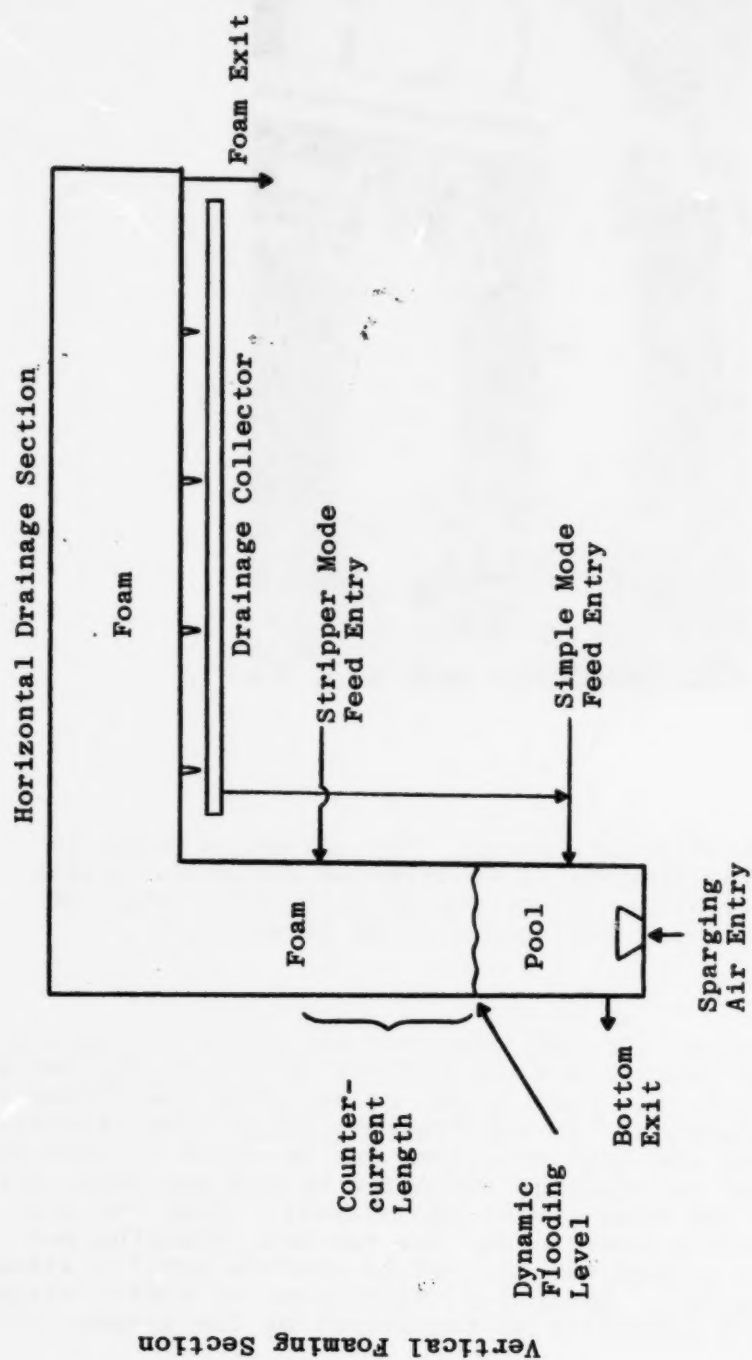


FIGURE 4
Column Nomenclature

level and steady rate of foam drainage return. As the foam proceeds up the vertical section, drainage returns counter-current to foam flow. In the horizontal section drainage is perpendicular to foam flow and is removed through valved ports in the bottom of the section (Figure 2). Drainage is collected in the drainage return pipe (Figure 2) and returned to the vertical section by gravity or pumping. Usually from one to two hours were required to reach steady state; separation results are based on samples taken at steady state.

Sparging Heads - Production of a stable and persistent foam is a fundamental requirement for achieving efficient separation of metal ions from acid mine drainage. Since the goals of separation are to decontaminate the feed and to collect the contaminating metal ions in as small a foam volume as possible, a foam of sufficient stability to allow protracted drainage is desirable. As a foam drains its persistence decreases due to thinning of bubble films. Thus in practice it is often difficult to separate foam drainage and bubble coalescence. Since the foam becomes progressively more susceptible to rupture as drainage proceeds, the drainage section of the column must reduce to a minimum the chances of physical shock. A horizontal drainage section provides a minimum countercurrent flow of interstitial liquid through the foam by allowing gravitational drainage perpendicular to foam flow instead of parallel through the length of the column. By reducing countercurrent drainage flow, the chances of bubble rupture are reduced especially at low foam densities. Drainage sections must be designed to provide minimum constriction or expansion of the drainage foam, and as smooth an inside surface as practical.

A foam is produced from a number of individual bubbles; however the structure of a foam is best visualized as a network of interconnecting films surrounding gas spaces. The pressure difference across a bubble film is

$$\Delta p = \frac{2\gamma}{r}$$

where γ is the surface tension and r is the radius of curvature. Thus it is evident that the pressure difference increases as the radius decreases. This explains the tendency for larger bubbles to grow at the expense of smaller ones in a foam of varying bubble sizes. A foam with a wide distribution of bubble sizes tends to be self destructive. As the bubbles rupture, surface adsorbed material is released into the interstitial liquid and the efficiency of separation is reduced. Thus it is necessary to produce a foam with as narrow a bubble size distribution as possible.

One practical method to produce a foam for continuous foam separation is by sparging air through an orifice(s) into a

liquid and have the foam form above the liquid. Since bubble size and size distribution are important to foam separation, considerable time was spent designing and testing sparging heads.

An explicit relationship for the bubble size obtained by sparging as a function of pore size, solution density and surface tension has not been determined for multi-pore devices. Thus, it is necessary to conduct experiments to find the sparging device most suited to the conditions.

Seven different sparging heads were constructed and tested. Two heads were made from glass Buechner style filtering funnels (Corning No. 36060) with 125 mm and 90 mm diameter fritted discs of coarse porosity. Porosity varied over the discs which resulted in channeling and thus streams of large bubbles. The small diameter disc produced less channeling, but still the bubble size distribution was too wide for a stable foam.

Three and four glass gas dispersing tubes (Corning No. 39533) with fritted cylinders of extra coarse porosity were mounted in specially constructed manifolds and adapted to the 6 in.-dia. column for use as sparging heads (Figure 5). The tube stems were shortened from 250 to 57 mm. These heads showed very little channeling and produced a stable foam.

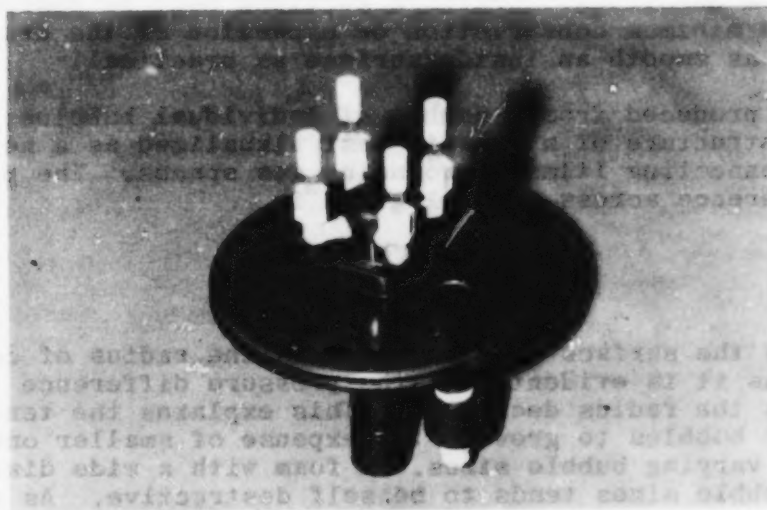


FIGURE 5. Sparging Head. The head is made from four pyrex gas dispersing tubes with extra coarse fritted cylinders. The diameter of the fritted cylinder is 2 mm. The support structure and a column adapter coupling is made of PVC and polyethylene plastic.

A special holder was fabricated from PVC plastic to hold 2 in.-dia. discs of scintered stainless steel (Pall Corp. Type 316L). Six porosity grades ranging from 5 to 165 μ mean pore size were tested and found to be less uniform and to channel more than the fritted glass discs in the Buchner funnels. The foam produced was very unstable.

A sparging head was fabricated from stainless steel to hold four cup-shaped spinnerettes which contained precision drilled holes on their upper faces. The spinnerettes were designed for previous unrelated research but were tested to determine if holes of one known size and spacing would produce a uniform, narrow bubble size distribution. The four spinnerettes had 60 holes (15 each) of 125 μ -dia. The bubbles formed were very uniform and the foam was stable. However, the sparging air capacity was too small for use in the 6 in.-dia. column. Quotes for fabrication of a larger sparging head of sufficient air capacity were approximately 1.5 dollars per hole. Since at least 2000 holes of 80 μ -dia. would be necessary, the cost of 3000 dollars was considered excessive at the present stage of research.

The same sparging head used to hold the spinnerettes was also used to hold discs of collimated hole structure (Brunswick Corp.). One disc contained 5,500 holes of 125 μ -dia. and the other contained 335,000 holes of 12.5 μ -dia; both discs were tested as currently available without special fabrication. Both discs produced streams of bubbles widely varying in size, not because of channeling but due to bubble coalescence in the swarm. The hole spacing (length between hole centers) is less than three hole radii apart; this allows for bubble coalescence and the resulting wide bubble size distribution and unstable foam. Collimated hole structure can be made in a wide variety of hole sizes and spacings and may be a less expensive alternative for drilled spinnerettes.

The results of the test indicate that the sparging head constructed of four dispersing tubes (Figure 5) is adequate for producing a reasonably stable foam; it was used in all subsequent tests. Its low cost is an attractive feature.

Feed Distributors - Operation of the foam column in the countercurrent mode requires that descending liquid feed be introduced into ascending foam without causing significant bubble rupture or liquid channeling. The feed stream must, therefore, impinge the foam stream with minimum momentum. Uniform distribution of the feed stream across the column diameter is desired to provide liquid-foam contact over a minimum downflow length. To meet these requirements, special liquid distributors were constructed and tested.

Previous work with countercurrent foam separation has lead to liquid distributors of various designs. Spaced, packed columns have been used to distribute feed streams (9). Distributors constructed of single tubes, multiple tubes and screen mesh in various configurations have been used (3) (21). In general, the multiple tube distributors are reported to have operated most effectively.

Three multiple tube distributors were designed, constructed, and tested with the 6 in.-ID column. Based on the expected liquid feed rates (approximately $500 \text{ ml} \cdot \text{min}^{-1}$), the number of distributor tubes of various sizes necessary to provide the required pressure drop, was calculated such that the feed liquid would impinge the foam at near ambient pressure. This would provide minimum momentum transfer to the foam and, thus, reduce foam collapse. The number of tubes should be sufficient to provide effective feed distribution over the column cross-section, but not so numerous that their cumulative surface area exposed to the foam would be large enough to disrupt foam flow. Based on these considerations, the three distributors had 8, 12 and 21 tubes each of 0.062 in.-ID, 0.045 in.-ID and 0.030 in.-ID tubing, respectively.

The distributors are constructed entirely of polyethylene tubing and silicon rubber potting material. The smaller distributing tubes are potted directly into 0.25 in.-ID tubing which connects directly to the feed stream tubing. The silicon rubber provided an economical and durable method for distributor construction.

While all three distributors operated satisfactorily, the 8-tube distributor caused some channeling, and the 21-tube distributor appeared to disrupt the foam flow more than the others. The 12-tube distributor provided adequate distribution with minimal channeling and foam collapse. The 12-tube distributor was used in all subsequent countercurrent experiments.

SECTION V

ANALYTICAL METHODS

Total Fe, Ca, Mg, Al and Mn - These metals in AMD are determined by atomic absorption spectrophotometry using standard comparator methods (31). The samples are aspirated directly into the flame with dilution necessary only to bring the samples into the concentration range of the particular resonance line. A high solids burner head (Perkin-Elmer three slot) is used and no interferences from the surfactant present has resulted.

Surfactant - Most of the surfactants used to date have been anionic and possess a sulfonate or sulfate hydrophylic group. Such surfactants form strongly colored complexes with the triphenylmethane dyes which thus provide the basis for a spectrophotometric method of surfactant determination (32). In this case, the dye crystal violet is complexed with the surfactant, the colored complex is extracted by benzene and the absorbance of the benzene layer determined at 615 mu.

Ferrous Iron - Since the Fe II/Fe III ratio present in mine water can theoretically have an effect on the foam separation of iron, determination of this variable was considered important. Fe(II) is determined spectrophotometrically (33), and Fe(III) is determined by difference from total iron determined by atomic absorption. Fe(II) in aqueous solution is complexed by 4,7-diphenyl-1-10-phenanthroline at pH 4, the colored complex is extracted by n-hexyl alcohol and the absorbance of the alcohol layer measured at 533 mu.

pH - The surfactants under test are weak acids and, thus, their solubility and speciation in solution is a function of pH. pH is monitored by a glass electrode - calomel reference electrode pair and a pH meter.

Bubble Diameter Measurement - As will be seen in Section VI, determination of the average bubble diameter in the foam is necessary for calculation of surface excess. Bubble diameters can be determined by direct or indirect methods. An example of an indirect method is the empirical relationship of optical density to bubble diameter. A direct measurement would be bubble photographs. It is known that photographs of a foam taken through a glass surface can yield useful measurements of bubble diameters (34). The bubble diameters at the periphery of the foam column are not significantly different from those in the interior. Thus a method of obtaining photographs of the bubbles was developed. A 35 mm

single-lens reflex camera with a bellows unit and 55 mm lens was used to obtain 1-2 x photographs of the moving foam. A strob-flash provided the light.

Bubble diameters are measured directly from the negative with an optical comparator which magnifies the bubbles and allows visual comparison of the bubble to a graduated reticle. The measured diameters, d_i are used to calculate a mean diameter,

$$\bar{d} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where n_i is the number of bubbles of various diameters d_i . Calculation of $\bar{d}$ was by computer.

SECTION VI

SAMD EXPERIMENTS - RESULTS AND DISCUSSION

Surfactant Screening - A great number of surfactants are commercially available from an equally great number of companies. Surfactants are commonly sold under trade instead of generic names because their chemical compositions are considered proprietary. In addition, test information on the chemical and physical properties of surfactants is often fragmentary and/or inconsistent or noncomparable from one manufacturer to another. Therefore, the screening of surfactants for those suitable to foam separation under the conditions encountered in acid mine drainage presents a formidable task.

Since the metal ions in acid drainage are not surface active, a surfactant must be added to allow coadsorption of metal. Coadsorption of metal may arise from charge interactions between adsorbed surfactant and a diffuse double layer of metal counterions, or from bonded interactions between surfactant and metallic species. Both methods for obtaining coadsorption have been considered.

Since the major metallic constituents of acid mine drainage, i.e., Fe, Al, Ca, Mg and Mn, occur as cations at low pH, an anionic surfactant would be required for coadsorption by the charge interaction mechanism. Thus, of the three charge types, i.e., nonionic, cationic, and anionic, anionic surfactant has received greatest attention.

Metal-ligand complexes of high bond strength and metal specificity are formed by a class of multidentate ligands known as chelates. Ethylenediamine tetraacetic acid (EDTA) and diethylene triamine pentaacetic acid (DTPA) (and their associated salts) are well known, examples of ligands which form water soluble, multidentate complexes (chelates) with a variety of metal ions. These chelates are characterized by exceptional complex stability and metal specificity; however they have minimal surface activity and are not directly useful in foam separation. The chelating ability of EDTA and the surfactant properties of the dodecyl-benzyl functional group are combined in dodecylbenzyl-diethylene triamine tetraacetic acid (DBDTTA) to form a water soluble, chelating surfactant. Another chelating surfactant is dodecylimino diacetic acid (DIDAA).

To screen the large number of available surfactants by laboratory experiments would be very costly in time. Thus,

an extensive literature search was considered the most practical method for picking the few best surfactants for laboratory testing. Research and commercial data was consulted; in addition, surfactant manufacturers and suppliers were consulted and asked to consider surfactant requirements and recommend suitable materials. By these methods surfactants were chosen for testing.

Anionic type surfactants were chosen which produce stable foams which have sufficient solubility at low pH and in hard water to resist precipitate and/or micelle formation and which are low cost and readily available. Unfortunately, chelating surfactants are not commercially available and can be obtained only in research quantities at considerable cost. Thus, the testing of chelating surfactants has not been further considered.

Surfactant Tests - The potential for effective foam separation can be expressed by the surface excess concentration Γ (equation 1, page 7) for surfactant and coadsorbants, in general the greater the Γ values, the greater the potential.

The equilibrium surface excess of a solute is usually determined by measuring surface tension as a function of solute concentration. Solute concentration is kept low so that the activity coefficient can be assumed equal to one and, therefore, the chemical activity is assumed the same as concentration. Γ values measured in this manner are not representative of dynamic foam separation systems (35) and, thus, have little value. Instead, useful equilibrium values can be determined for surfactant and coadsorbed metals under dynamic conditions in a foam column designed for that purpose. The equilibrium column (Figure 3) was designed to allow measurement of Γ values. The column operates in the continuous, simple mode.

By mass balance and surface equilibrium considerations around the foam, the system can be described by

$$[x]_c L_c = [x]_b L_c + \frac{6G\Gamma_x}{\bar{d}} \quad (2)$$

where $[x]$ is the concentration of surfactant or coadsorbed component

L_c is the liquid volume rate of foam

G is the air volume sparging rate

$\bar{d}$ is the average bubble diameter

Γ_x is the surface excess in equilibrium with $[x]_b$

and the subscripts c and b refer to the foam exit and pool exit flows, respectively.

Rearrangement of equation (2) gives an expression for Γ_x

$$\Gamma_x = ([x]_c - [x]_b) \frac{\bar{d} L_c}{6G} \quad (3)$$

Thus, by measuring $[x]_c$, $[x]_b$, $\bar{d}$, L_c and G , values of Γ_x can be calculated for x equal to surfactant, Fe, Ca, Al, Mn and Mg. The basic requirement is that sufficient bubble liquid contact time be provided to assure attainment of surface adsorptive and coadsorptive equilibrium and that foam coalescence is minimal. Such equilibria appear to have rapid kinetics (36), and approximately one foot of pool depth gives sufficient bubble contact time (29).

Five surfactants, determined in the initial screening to have properties suitable for foam separation at low pH, were selected for testing. The tests were carried out in the equilibrium column to determine Γ values for surfactant and metal constituents. Each of the surfactants were tested at four feed concentrations ranging from 100-400 ppm in standard SAMD.

The surfactants tested were sodium dodecyl sulfate, Alkanol 189-S (DuPont), Alipal EO-526 (GAF), Alipal CD-128 (GAF) and Aerosol AY (Cyanamid). Alkanol 189-S is a sodium alkyl sulfonate with an average carbon chain length of 15. Alipal EO-526 is a sodium salt of a sulfated alkylphenoxy poly(ethyleneoxy) ethanol with an undisclosed chain length. Alipal

CD-128 is a sulfate-ester type surfactant based on a linear chain (hydrophobe) of undisclosed length. Aerosol AY is sodium diamyl sulfosuccinate.

Upon addition of Alkanol 189-S to SAMD, a coarse reddish precipitate formed. Alkanol 189-S is normally a high foaming, acid stable surfactant, but mixed with SAMD it produced only a transient froth. A sample of the precipitate was dried at 100°C, producing a viscous substance obviously containing a large amount of surfactant. The surfactant is incorporated in the precipitate and the precipitate is not solely the result of oxidation of Fe(II) and hydrolysis of Fe(III) due to pH increase.

Aerosol AY would not produce a stable foam in SAMD over a concentration range of 100-500 ppm surfactant.

In the tests using sodium dodecyl sulfate, Alipal EO-526, and Alipal CD-128, stable foams were produced and the data necessary for Γ calculations were obtained.

For purposes of surfactant comparison, individual Γ values for surfactant and SAMD metals were averaged for each surfactant and surfactant concentration; the results are in Table 2.

TABLE 2

Dynamic Surface Excess Values for
Selected Surfactants in SAMD

Equilibrium Column, $G = 10 \text{ liters} \cdot \text{min}^{-1}$
 $L_f = 700 \text{ ml} \cdot \text{min}^{-1}$, $[S]_f = 100\text{-}400 \text{ ppm}$

Surfactant, S	Γ_s	Γ_{Fe}	Γ_{Ca}	Γ_{Mn}	Γ_{Mg}	Γ_{tm}	Γ_{tm}/Γ_s
(Units: $\times 10^{11} \text{ moles} \cdot \text{cm}^{-2}$)							
Sodium dodecyl sulfate, NaDS (M.W. = 288)	26.1	5.22	5.11	0.131	0.768	11.2	0.430
Alipal EO-526 (M.W. = 586)	27.7	3.22	1.92	0.1	0.166	5.40	0.195
Alipal CD-128 (M.W. = 352)	48	2.5	1.5	0.14	0.99	5.09	0.106
Aerosol AY (M.W. = 360)	No foam produced over surfactant concentration range 100-500 ppm						
Alkanol-189S (M.W. = 354)	Precipitate formed; only transient foam produced						

The economics of foam separation are greatly dependent on the magnitudes of the adsorptive Γ for surfactant and the coadsorptive Γ for the metals to be separated. Increased adsorption of surfactant to bubble walls increases the capacity to separate coadsorbed metals and thus promotes the most efficient use of surfactant. Because foam separation is inherently of low exchange capacity compared to ion exchange or solvent extraction (1), the economics of foam separation will depend on maximizing exchange capacity (i.e., maximizing coadsorptive) per consumption of materials and power (i.e., surfactant and sparging air).

Generally a stoichiometric relationship is believed to exist for foam separation of dissolved constituents, but the exact relationship has not been clearly defined. In foams produced from pure aqueous solutions of ionic surfactants, the surface concentrations of adsorbed surfactant and coadsorbed metal will be equal (1), e.g., for NaDS in deionized water $\Gamma_{Na^+} = \Gamma_{DS^-}$ and the ratio $\Gamma_{Na^+} / \Gamma_{DS^-} = 1$. Considering metal coadsorption to arise from charge interactions with adsorbed surfactant, and considering the requirement of electroneutrality for the system, a one-to-one ratio of surfactant and metal in the foam would be expected on an equivalent basis. Ratios less than one indicate coadsorptive competition from metal impurities.

At a pH of 2.2, the hydrogen ion concentration in SAMD is $6.3 \times 10^{-3} M$ compared to about $7 \times 10^{-3} M$ total added metal. Sodium in SAMD derived from surfactant and tap water (approximately 13 ppm in tap water) is at least equal molar with surfactant (sodium analyses were not conducted). Iron in SAMD is initially greater than 98 percent Fe(II); the extent of oxidation to Fe(III) during sparging and, thus the exact equivalence of iron in the foam system is unknown. For these reasons, equivalence ratios of coadsorbed metal to adsorbed surfactant are not determined. Molar ratios are used to provide information on the relative effectiveness of a particular surfactant for foam separation in standard SAMD.

An optimum value for adsorptive Γ , the value to which experimental values for surfactants can be compared, can be estimated at least as to order of magnitude (1). A Γ value of about $3 \times 10^{-10} \text{ moles} \cdot \text{cm}^{-2}$ would be expected under equilibrium conditions for the surfactant sodium dodecyl sulfate (M.W. = 288). Comparing the average Γ_s values in Table 2 with this theoretical value, it is apparent that adsorptive equilibrium was reached for NaDS, EO-526 and CD-128. Considering the individual surface excess values for each metal Γ_m , and then the sum of the individual values

Γ_{tm} , it is clear that NaDS with a molar ratio of total coadsorbed metal to adsorbed surfactant Γ_{tm}/Γ_s equal to 0.430 is the most efficient surfactant for metal separation.

Effect of pH - Experiments were conducted at pH 2.4, 2.7 and 2.9 to determine the effect of hydrogen ion concentration on foam separation of SAMD metals with NaDS. pH was adjusted from 2.2 with NaOH, the upper limit being restricted by iron precipitation at about pH 3.0. The results in Table 3 indicate a slight decrease in Γ_s and a more significant decrease in Γ_{tm} with increasing pH. The decrease in Γ_{tm} and Γ_{tm}/Γ_s results mostly from decreased coadsorption of iron.

TABLE 3

Effect of pH on Metal Separation from SAMD

Equilibrium Column, $G = 10 \text{ liters} \cdot \text{min}^{-1}$

$L_f = 700 \text{ ml} \cdot \text{min}^{-1}$, $[S]_f = 100 \text{ ppm}$

pH	Γ_s (Units: $\times 10^1$	Γ_{mt} moles $\cdot \text{cm}^{-2}$)	Γ_{mt}/Γ_s
NaDS and SAMD			
2.2	2.61	1.12	0.430
2.4	2.40	1.08	0.450
2.7	2.22	0.761	0.343
2.9	2.34	0.542	0.232
EO-526 and SAMD without iron			
2.8	1.56	0.303	0.194
3.5	1.52	0.212	0.139
4.4	1.41	0.202	0.143

Three additional experiments were conducted over a wider pH range at 2.8, 3.5 and 4.4 with EO-526 and SAMD without iron. The results in Table 3 also indicate a slight decrease in Γ_s and a more significant decrease in Γ_{tm} . The relative decrease of Γ_{tm} with pH is greater with iron present.

Effect of the Chelating Agent EDTA - A number of experiments were conducted to determine the effect of the chelating agent EDTA on the coadsorption of metals in SAMD with both anionic and cationic surfactants. EDTA alone will not produce a foam in SAMD, but in combination with a surfactant it is possible that its ability to form strong, selective, ionic metal complexes coupled with its tendency to associate with and stabilize foams could enhance selective foam separation of metals. The stability of EDTA complexes with SAMD metals is: $\text{Al} > \text{Fe(II)} > \text{Mn} > \text{Ca} > \text{Mg}$. In general, except for the alkaline earths, the metal chelates are stable to a pH of near 1.0. Decreasing pH favors formation of less highly ionized, less strongly chelated complexes. The effect of increasing pH is to stabilize the completely ionized chelated species, but at high pH this advantage is balanced and eventually nullified by metal hydroxide formation.

Three experiments using NaDS and SAMD at pH 2.3 were conducted with EDTA to NaDS molar ratios of 0.59, 1.02 and 1.62; $[\text{NaDS}]_f$ was $4.38 \times 10^{-4} \text{ M}$. Γ_s for the three experiments was 1.82×10^{-10} ; for Γ_{tm} it was 3.51×10^{-11} which gives a Γ_{tm}/Γ_s ratio of 0.193. Comparing these values to those in Table 2 for similar conditions except without EDTA, it is apparent that adsorption of surfactant and coadsorption of metal is reduced by EDTA.

Six additional experiments were conducted to test higher concentrations of EDTA with both anionic NaDS and cationic Hyamine-1622 surfactants. Hyamine-1622 (Rohm and Haas) is di-isobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, monohydrate. These experiments were conducted under conditions similar to those above except with an EDTA to total SAMD metal ratio of 1 and pH at 2.9 - 3.1, 6.0 - 6.2 and 7.8 - 7.9. In three experiments $[\text{NaDS}]_f$ was $6.89 \times 10^{-4} \text{ M}$; in the other three $[\text{Hyamine-1622}]_f$ was $7.22 \times 10^{-4} \text{ M}$.

At pH 7.8 - 7.9 Hyamine-1622 and SAMD produced a dark red-brown turbid solution containing a grey-black precipitate; at pH 6.0 - 6.2 the solution was yellow-green and turbid; at pH 2.9 - 3.1 the solution was green and clear. In all three pH ranges foam production and stability was marginal; and no measurable amounts of metal were removed.

With NaDS and EDTA, metal separation at all three pH ranges was lower than without EDTA as indicated by Γ_{tm}/Γ_s ratios of less than 0.190. The results of these tests indicate no enhancement of metal coadsorption with EDTA compared to surfactant alone. Hyamine-1622 partially precipitated with

SAMD and EDTA, thus results from its tests were questionable. The possibility of enhanced separation and metal specificity with chelating surfactants remains to be examined.

Effect of Surfactant Concentration - Results of testing several surfactants in SAMD at various pH values with and without EDTA indicate that NaDS without EDTA at the 2.2 - 2.3 pH of standard SAMD are the most efficient conditions tested. Therefore, NaDS was used in all subsequent experiments.

The Γ_s values for a surfactant will increase with surfactant concentration until complete saturation of the air/solution interface is reached. Further increase of surfactant concentration will not increase Γ_s . As surfactant concentration increases the critical micelle concentration (CMC) is reached, above which additional surfactant will form micelles which are bulk rather than surface active. Above the CMC, the Γ_s for surfactant will remain constant while the Γ_{tm} for coadsorbed metal will decrease due to coadsorption competition between surfactant adsorbed at bubble interfaces and surfactant present as micelles. The maximum surfactant concentration for efficient coadsorptive separation will be determined by the CMC and/or the concentration at which surface saturation is maximum (theoretically these two concentrations are the same). The lower limit of surfactant concentration is usually that necessary to produce a stable foam. Thus, an optimum surfactant concentration or concentration range will exist at which maximum coadsorptive separation of metal will be achieved.

SAMD was foamed in a series of experiments with NaDS over a surfactant feed concentration range of 180-300 ppm. The column was operated in the simple continuous mode with an extended horizontal drainage section. A second series of experiments were conducted under similar conditions but with a more dilute mine drainage DSAMD, the composition of which is given in Table 4. For reasons of analytical sensitivity, the metal concentrations are not in the same relative proportions as in SAMD. The results are shown in Figure 6.

The distribution coefficients for both SAMD and DSAMD, which differ by a factor of approximately 200 in total molar metal concentration, indicate the optimum $[\text{NaDS}]_b$ is in the range 4.7 to $6.1 \times 10^{-4} \text{ M}$.

TABLE 4
Dilute SAMD

Constituent	Metal Concentration, M x 10 ⁶
FeSO ₄ · 7H ₂ O	2.24
CaSO ₄ · 2H ₂ O	11.5
MgSO ₄ · 7H ₂ O	1.42
MnSO ₄ · H ₂ O	0.574
Al ₂ (SO ₄) ₃ · 18H ₂ O	20.4

Effect of Countercurrent (Stripping Mode) Column Operation -
Two series of experiments were conducted with SAMD under conditions similar to those reported in Figure 6 except that the column was operated in the stripping instead of the simple mode. Two countercurrent lengths were tested to determine the effect on separation of increased contact time between counterflowing feed and foam. [NaDS]_f was set such that [NaDS]_b would be in the optimum range (Figure 6).

For comparison, results of the stripping experiments are shown in Table 5 with those from an analogous experiment conducted in the simple mode. Extension of the countercurrent length from 15 to 29 inches produced an absolute increase in both surfactant adsorption and metal coadsorption; however, the relative metal coadsorption per unit surfactant adsorbed remained the same. Comparison of Γ_{tm}/Γ_s and VR values for stripping and simple operation suggests the stripping mode to be less efficient at metal separation. Greater liquid carry-over with countercurrent operation would be expected considering the higher adsorbed and interstitial liquid surfactant concentrations compared to simple operation. Extension of the horizontal drainage section would increase VR to about 20 without significant reduction in separation due to foam collapse.

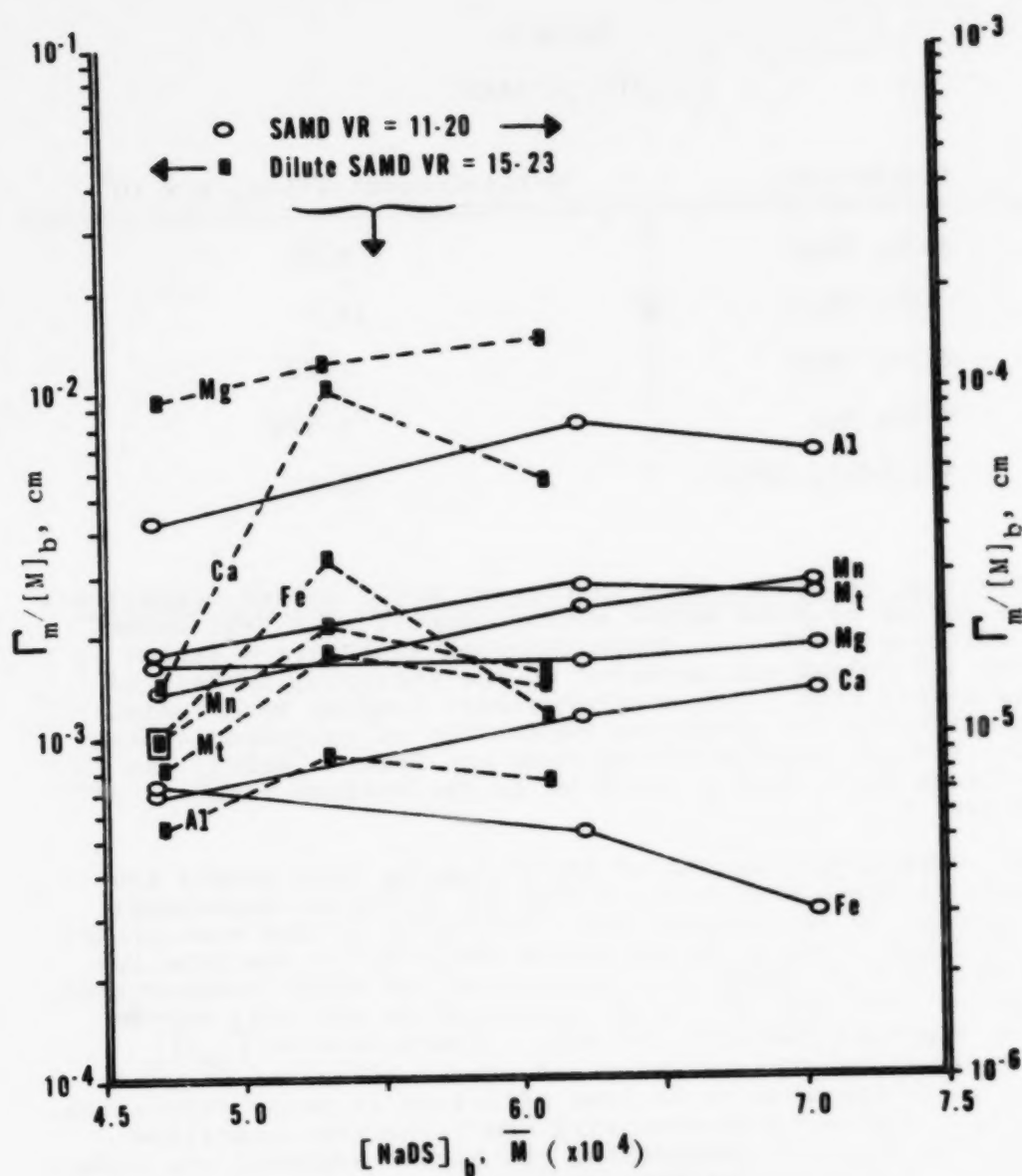


FIGURE 6 DISTRIBUTION RATIOS
 Simple Mode, 18 in. Vertical Section, 72 in. Horizontal Section,
 $G = 8 \text{ liter} \cdot \text{min}^{-1}$, $L_f = 500 \text{ ml} \cdot \text{min}^{-1}$. Each data point
 represents the average of 4 to 5 measurements.

TABLE 5

Comparison of Simple and Stripper Mode Experiments*
(SAMD and NaDS, $G = 8 \text{ liter} \cdot \text{min}^{-1}$, $L_f = 500 \text{ ml} \cdot \text{min}^{-1}$)

Variable	Stripper	Stripper	Simple
Column Mode			
Vert. Sect., in.	24 in.	36 in.	18 in.
Horz. Sect., in.	72 in.	72 in.	72 in.
C.C. Length, in.	15 in.	29 in.	-
VR	13.6	14.2	19.0
FRT, min.	6.02 min.	5.94 min.	5.99 min.
Γ_{tm} , moles $\cdot \text{cm}^{-2}$	9.06×10^{-11}	10.3×10^{-11}	11.1×10^{-11}
Γ_s , moles $\cdot \text{cm}^{-2}$	2.30×10^{-1}	2.70×10^{-1}	2.22×10^{-1}
Γ_{tm}/Γ_s	0.394	0.381	0.500

* Because adsorptive phenomena are in equilibrium with feed, liquid in the stripping mode rather than pool liquid as in the simple mode, the proper form of equation 3 for calculation in the stripper mode is (29):

$$\Gamma_x = ([X]_c - [X]_f) \frac{\bar{d} L_c}{6.59 G}$$

In the simple mode, adsorptive phenomena are in equilibrium with pool liquid; in the stripping mode equilibrium is with feed liquid. Since surfactant optimization tests (Figure 6) were conducted in the simple mode, and since $[\text{NaDS}]_f$, $[\text{NaDS}]_b$, the surfactant concentration in the stripping tests was above optimum for maximum coadsorption of metal. A reduction of $[\text{NaDS}]_f$ from $8.7 - 8.9 \times 10^{-4} \text{ M}$ to $4.7 \times 6.1 \times 10^{-4} \text{ M}$ would increase Γ_{tm}/Γ_s to about 0.5 and thus increase separation by about 3 to 21 percent. The small relative magnitude of this increase with respect to metal separation from SAMD precluded allocation of time for further tests.

Volume Reduction - Production of dry foams is required to reduce interstitial liquid carry-over in the foam and, thus, to reduce the waste volume for a foam column operating to decontaminate the feed. Volume reduction factors (L_f/L_c) were determined as a function of sparging rate G and surfactant concentration (Figure 7). Volume reduction factors equivalent to approximately 1.7 to 3.8 percent liquid carry-over are easily achieved at low gas rates. Further increase in volume reduction factors may be possible through increase of foam residence time FRT which is accomplished by reducing sparging rate and/or by lengthening the drainage section.

The practical factors which operate to limit volume reduction in a 6 in.-dia. column are the sparging heads at high gas rates and foam collapse at low gas rates, i.e., long FRT. At high gas rates, bubble diameters increase and their size distribution widens. Thus surface throughput per volume of gas and foam stability declines markedly. At low gas rates a maximum FRT is reached above which further drainage to reduce interstitial liquid results in foam collapse and reduction in separation efficiency. With protracted drainage the foam becomes dry and its susceptibility to rupture increases until mechanical shock from flow in contact with the column wall produces complete collapse.

The inverse log relationship of foam density and drainage time (1) and the practical limits for foam drainage in the 6 in. column are shown in Figure 8. For $[NaDS]_f = 200$ ppm the foam density decreases with drainage for FRT values approximately three and greater; this section of the curve follows the expected exponential relationship. At low FRT values, which result experimentally from high sparging rates, the average bubble diameter is increased and the diameter size distribution is widened. The result is more rapid drainage and a significant reduction in foam stability. Also, at high gas rates turbulence in the pool causes voids to form in the foam at the foam-liquid interface. These voids progressively enlarge and destroy plug flow in the drainage section. The low foam densities at low FRT values (Figure 8) are caused by extensive foam collapse which, of course, destroys separation efficiency. The destructive effect of high sparging rates can be seen in Figure 7 where the curve of decreasing VR_1 with increasing gas rate changes shape above 10 liters·min⁻¹.

These data indicate the operational restrictions for the 6 in.-dia. column. A minimum surfactant concentration is required for foam production; under present conditions the minimum can be expressed as 100 ppm $\leq [NaDS]_f \leq 200$ ppm. Gas rates of approximately 10 liters·min⁻¹ or less are required with the EC fritted glass sparging heads. With these restriction foam densities in the range of $2 - 5 \times 10^{-3}$ ml liquid per ml

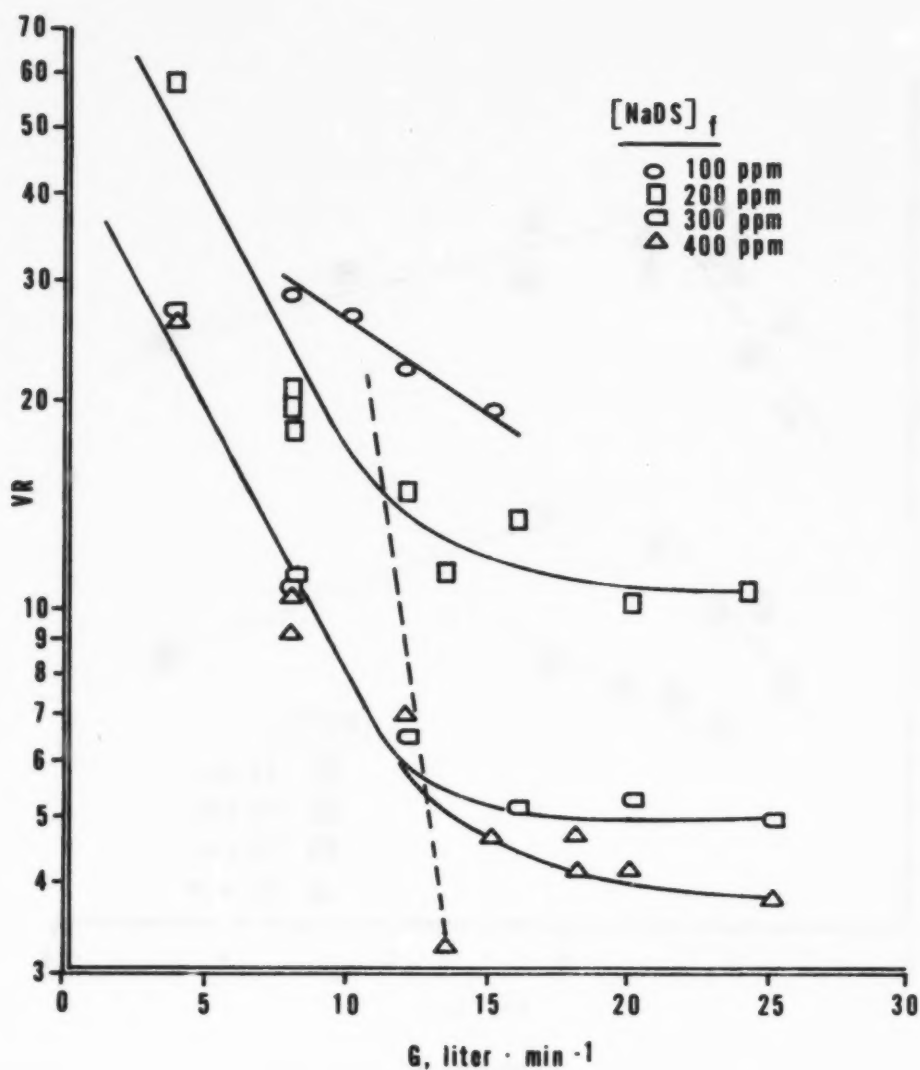


FIGURE 7
Volume Reduction versus Sparging Rate
 (Simple Mode, 18 in. Vertical Section, 36 in. and 72 in. Horizontal Sections,
 $L_f = 500 \text{ ml} \cdot \text{min}^{-1}$)

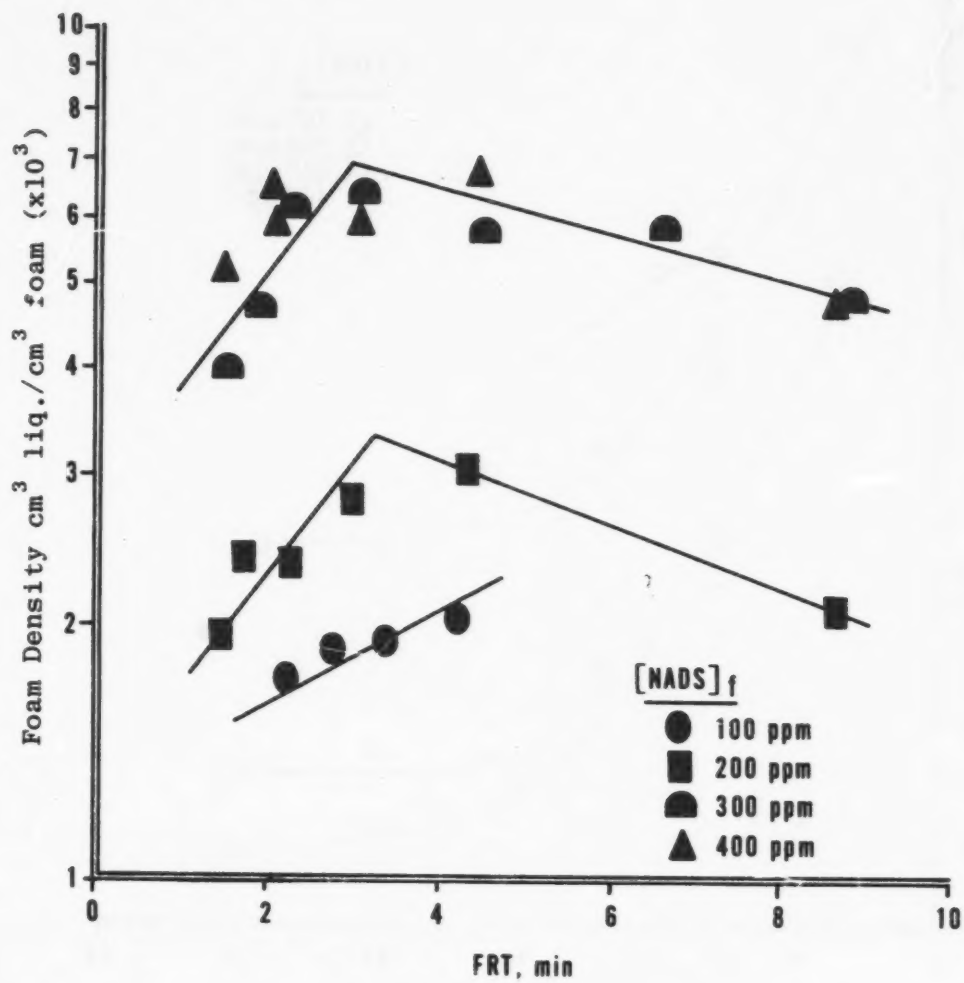


FIGURE 8
Foam Density versus Foam Residence Time

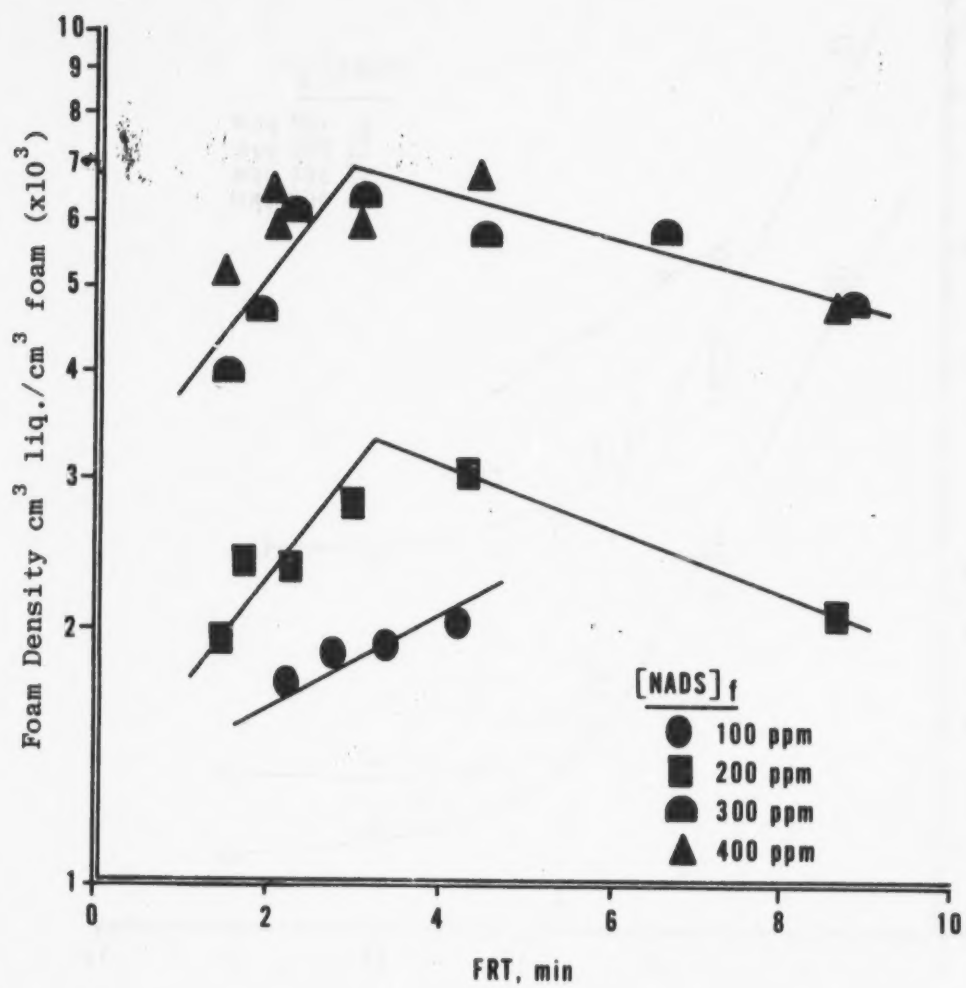


FIGURE 8
Foam Density versus Foam Residence Time

foam can be easily obtained; lower values could result from further development of drainage sections. However, since drainage rate and extraction rate are opposite functions of bubble diameter, a compromise must be made between separation efficiency and foam density. For this study the controlling factor is the narrow range of sparging rates over which a stable foam can be produced, the sparging head determining the upper limit and a minimum gas flow to produce a stable foam determining the lower limit.

Effect of Metal Concentration on Coadsorptive Separation -

In the presence of dissolved electrolytes, the surface tension and critical micelle concentration of ionic surfactants are reduced. Ions of charge opposite to the surface active species tend to reduce repulsion between surfactant ions and allow closer packing of surfactant in the surface film. Thus, the presence of cations in solutions of anionic surfactants, e.g., SAMD and NaDS, should tend to increase Γ_s values. Experimental data showing this effect is plotted in Figure 9; Γ_s values tend to be greater in SAMD than in DSAMD.

As shown in Figure 6, the decline in $\Gamma_{tm}/[M]_b$ with increasing $[NaDS]_b$ indicates that the CMC is reached at $[NaDS]_b$ greater than approximately $6 \times 10^{-4} M$ which is equivalent to $[NaDS]_f$ greater than $7.5 \times 10^{-4} M$ under the operating condition shown. The reduction in CMC by dissolved salts is evident by comparing these values to $7 \times 10^{-3} M$, the CMC for NaDS in pure aqueous solution (4).

Literature data for surface excess of NaDS in pure aqueous solution as measured by the foaming method is included in Figure 9 (4)(37). This data suggests that Γ_{NaDS} in SAMD would be larger than $3 \times 10^{-1} \text{ moles} \cdot \text{cm}^{-2}$ and possibly larger than $4 \times 10^{-1} \text{ moles} \cdot \text{cm}^{-2}$. Our data (Figures 6, and 9) show that practical Γ_{NaDS} values equal to $2-3 \times 10^{-1} \text{ moles} \cdot \text{cm}^{-2}$ are the equilibrium values for conditions in the 6 in. column. As indicated above (Figure 6), the foam column is most efficiently operated with a surfactant concentration below the CMC and with the concentration optimized for metal coadsorption under existing conditions.

Coadsorptive Γ values for total metals show the characteristic equilibrium relationship with increasing metal concentration in the pool (Figure 9). The total metal Γ values increase by a factor of approximately 10 while total metal concentration in the pool increases by a factor of 700; surfactant Γ values increase by a factor of 3 or less over the same increase in metal concentration.

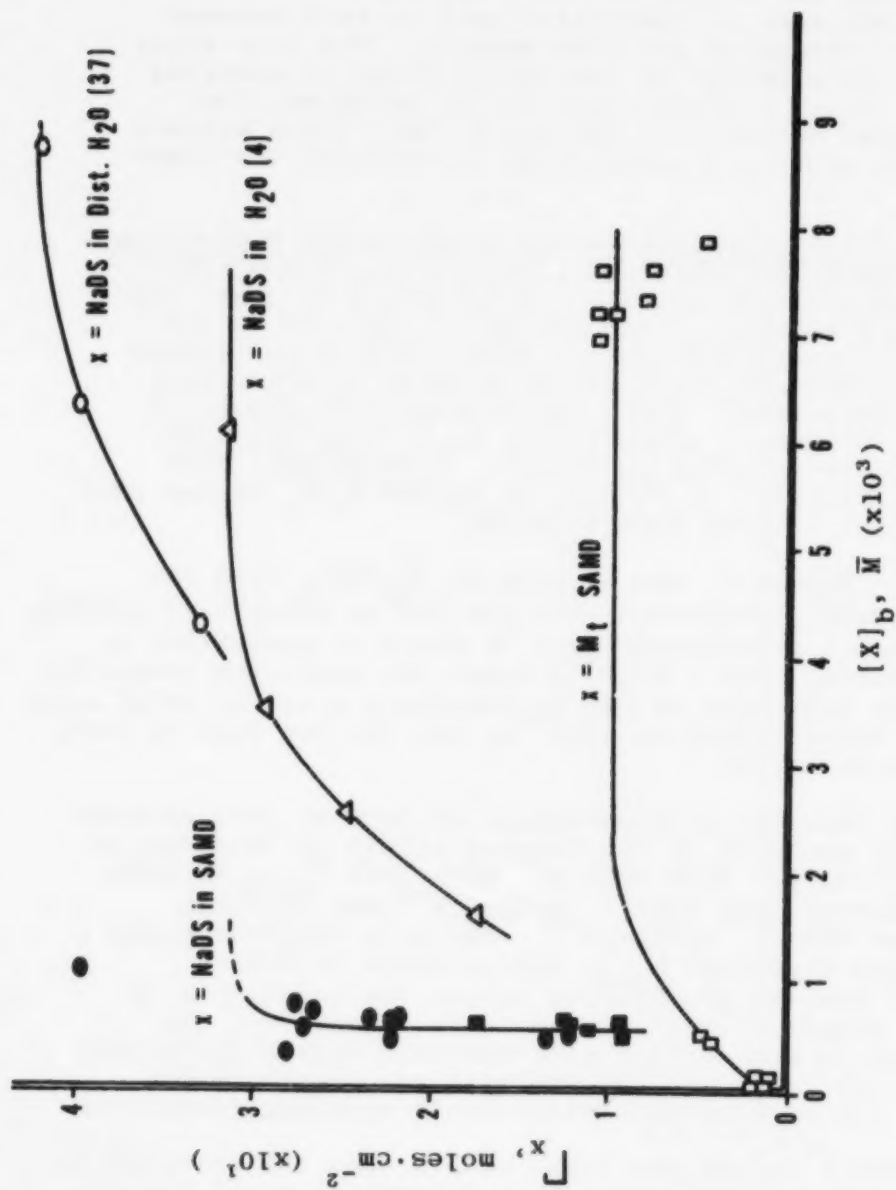


FIGURE 9
 Dynamic Surface Excess versus Pool Concentration
 (For $x = \text{NaDS in SAND}$: $\bullet$ is Dilute SAND, $\bullet$ is SAND)

Optimum Operating Conditions for the 6 in.-Dia. Column -
 The metal separation rate increases with higher metal feed rates (Figure 10) as would be expected from t_m data (Figure 9); the separation rate increases by a factor less than 5 while the metal feed rate increases by a factor of about 200. Optimum surfactant feed concentrations were found to have a narrow range over the wide range of total metal concentrations in SAMD and dilute SAMD (Figure 6). Thus, the range of surfactant feed rates (approximately $3.5 - 4.5 \times 10^{-4}$ moles $\cdot$ min $^{-1}$) was considerably narrower than the metal feed rates.

Data in Figure 10, which includes all simple and stripping experiments with standard and dilute SAMD, shows that the metal separation rates do not significantly differ as a function of operating mode and surfactant type (CD-128 and EO-526 experiment are included). The fraction of total metal removed depends strongly on the metal feed rate. For standard SAMD, an average metal separation rate is about 3.5×10^{-5} moles $\cdot$ min $^{-1}$ which is equivalent to 1.93×10^{-7} moles $\cdot$ cm $^{-2}$ of column cross section area per minute or approximately 4.0×10^{-7} equivalent cm $^{-2}\cdot$ min $^{-1}$. The corresponding experimental rate for surfactant is 4.8×10^{-7} equivalent cm $^{-2}\cdot$ min $^{-1}$. The difference between total metal and surfactant capacities represents unaccounted metal coadsorption such as from sodium derived from surfactant and metal impurities.

Based on theoretical calculations (1) and empirical measurements (4) the maximum exchange capacity for a foam separation system would be approximately 3×10^{-6} equivalent cm $^{-2}\cdot$ min $^{-1}$ based on an optimum bubble diameter of 0.08 cm, a maximum gas rate of 9.4 cm $^3\cdot$ min $^{-1}$ per cm ^{2} of column cross section and a packing density of 40 sq-Å per NaDS molecule on the bubble surface. This theoretical maximum sparging rate is equivalent to 1.7×10^{-1} cm $^3\cdot$ min $^{-1}$ for the 6 in.-dia. column and is 2.1 times larger than the practical rate of 8×10^{-1} cm $^3\cdot$ min $^{-1}$ which was restricted by foam instability at high rates using the EC fritted glass sparging heads. The average bubble diameter obtained in this study at gas rates of 8×10^3 cm $^3\cdot$ min $^{-1}$ was 0.13 cm and would reduce the surface area throughput by a factor of 1.6.

The 6 in.-dia. column operates at a practical capacity of 16 percent of theoretical. Improvement in sparging head design, possibly the use of precision drilled spinnerettes, or change in the method of sparging, such as bubble

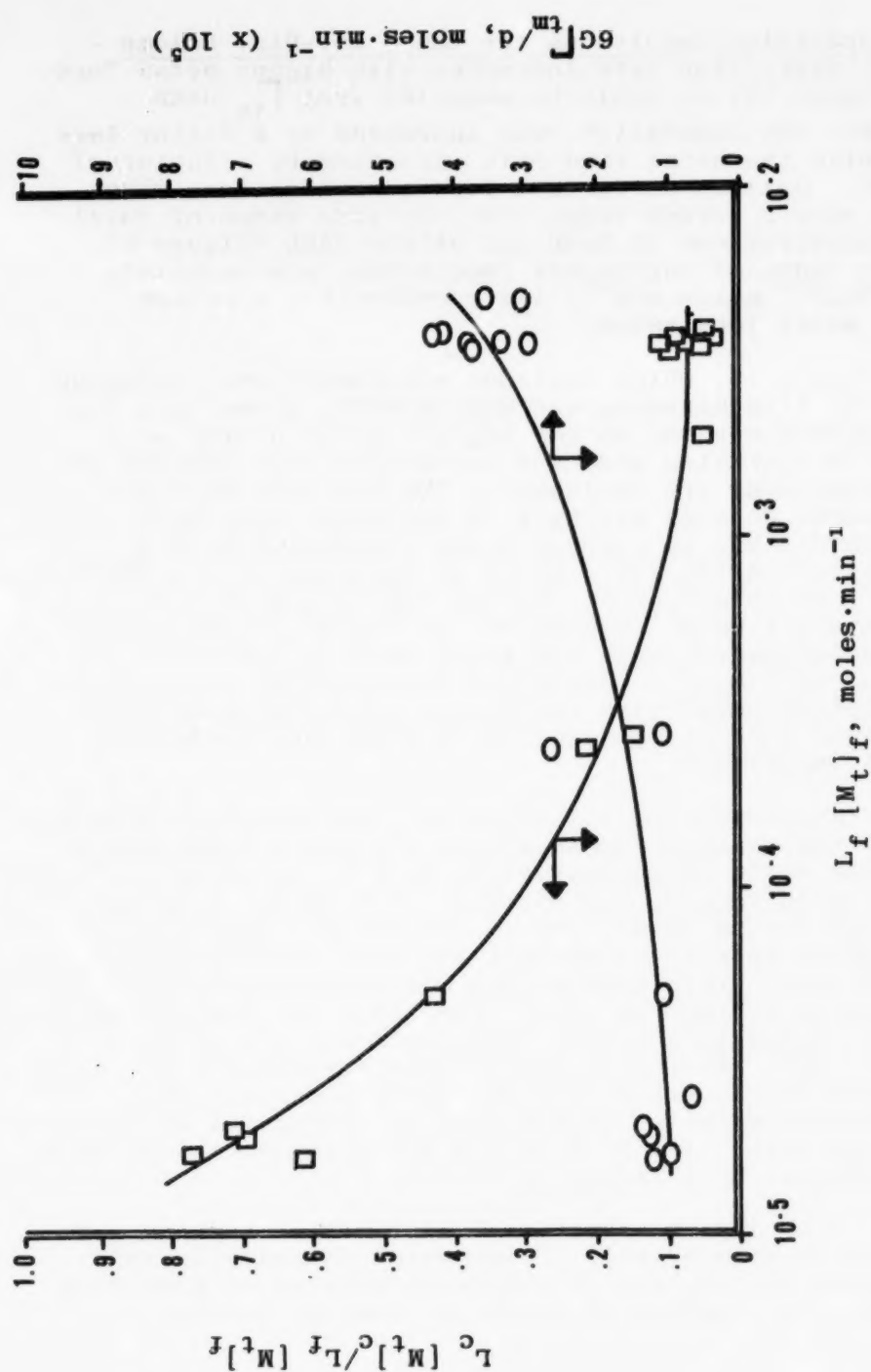


FIGURE 10
Total Metal Fraction Removed and Total Metal Extraction Rate Versus Total Metal Feed Rate.

formation by degasification of supersaturated solutions, may allow closer approach to optimum gas rates and bubble diameters. Allowing these improvements, the capacity would increase to 54 percent of theoretical.

Derived from the experimental results with SAMD, the optimum conditions for practical operation of the 6 in.-dia. column demonstrate the effectiveness of continuous foam separation for treating acid mine drainage (Table 6). Average values for VR, $[\text{NaDS}]_b$, $[\text{M}_t]_f$, SR_s and SR_{tm} determined within the practical operating values for G and L_f in the 6 in.-dia. column were used to calculate the average material balances for all SAMD experiments. Approximately 6 percent metal removal with 5 percent liquid carryover indicates that 1 percent metal is separated as coadsorbed metal. Twenty-six percent of the added surfactant is removed in the foam, 23 percent is removed as adsorbed material and 74 percent remains in the bottoms stream.

TABLE 6

Summary of Results for SAMD Experiments
and Comparison with AMD Experiments

Column Mode	SAMD and NaDS		AMD and NaDS (3 runs)	
	Simple and Stripping	Simple	Simple	Stripping
G, liter·min ⁻¹	8	4	8	8
L_f , ml·min ⁻¹	500	250	500	500
VR	20	27(11)	13	23
$[\text{NaDS}]_b$, moles·liter ⁻¹	6.0×10^{-4}	5.4×10^{-4}	4.8×10^{-4}	5.3×10^{-4}
$[\text{M}_t]_f$, moles·liter ⁻¹	7.0×10^{-3}	7.9×10^{-3}	7.5×10^{-3}	7.9×10^{-3}
SR_s , moles·min ⁻¹	8.8×10^{-5}	4.3×10^{-5}	7.3×10^{-5}	2.8×10^{-5}
SR_{tm} , moles·min ⁻¹	3.5×10^{-5}	1.7×10^{-5}	4.3×10^{-5}	1.8×10^{-5}
$[\text{NaDS}]_f$, moles·liter ⁻¹	7.7×10^{-4}	7.5×10^{-4}	7.1×10^{-4}	7.4×10^{-4}

TABLE 6 (continued)

	SAMD and NaDS	AMD and NaDS (3 runs)		
$[\text{NaDS}]_c$, moles.liter ⁻¹	4.1×10^{-3}	5.2×10^{-3}	2.4×10^{-3}	1.8×10^{-3}
$[M_t]_b$, moles.liter ⁻¹	6.9×10^{-3}	7.7×10^{-3}	7.4×10^{-3}	7.8×10^{-3}
$[M_t]_c$, moles.liter ⁻¹	8.3×10^{-3}	9.6×10^{-3}	8.6×10^{-3}	8.6×10^{-3}
R_{fs} , moles.min ⁻¹	3.8×10^{-4}	1.9×10^{-4}	3.5×10^{-4}	3.7×10^{-4}
R_{bs} , moles.min ⁻¹	2.8×10^{-4}	1.2×10^{-4}	2.2×10^{-4}	2.7×10^{-4}
R_{cs} , moles.min ⁻¹	1.0×10^{-4}	5.2×10^{-5}	9.0×10^{-5}	4.0×10^{-5}
R_{ftm} , moles.min ⁻¹	3.5×10^{-3}	2.0×10^{-3}	3.7×10^{-3}	3.9×10^{-3}
R_{btm} , moles.min ⁻¹	3.3×10^{-3}	1.7×10^{-3}	3.4×10^{-3}	4.0×10^{-3}
R_{ctm} , moles.min ⁻¹	2.0×10^{-4}	8.9×10^{-5}	3.2×10^{-4}	1.9×10^{-4}
Material Balance				
Metal, % diff.	-	7	1	8
H ₂ O, % diff.	-	5	0.4	6
NaDS, % diff.	-	9	13	16
SR_{tm}/SR_s	0.40	0.40	0.59	0.62
$SR_s/R_{fs} \cdot 10^2$	23%	23%	21%	7.7%
$R_{bs}/R_{fs} \cdot 10^2$	74%	63%	63%	73%
$R_{cs}/R_{fs} \cdot 10^2$	26%	27%	26%	11%
$R_{ctm}/R_{ftm} \cdot 10^2$	6.0%	4.5%	8.6%	4.8%
SR_{tm}/R_{ftm}	1.0%	0.85%	1.2%	0.45%

SECTION VII

AMD EXPERIMENTS-RESULTS AND DISCUSSION

To verify the results with SAMD, AMD was foamed with NaDS in the 6 in.-dia. column operating in both simple and countercurrent modes. The AMD originated from Grassy Run (Sample Site GT6-1) near Elkins, W. Va. and was trucked to Cleveland; the tests began approximately 24 hours after sampling. Analyses of the water was conducted approximately 30 hours after sampling (Table 7).

TABLE 7

Grassy Run Acid Mine Discharge (GT6-1)

Total Fe	112	ppm
Ca	114	ppm
Mg	32	ppm
Mn	3.8	ppm
Al	34	ppm
pH	2.75	

Two simple mode experiments at different liquid feed and air sparging rates were conducted on the second and third days after delivery of the Grassy Run AMD. The results of these experiments compare favorably with those using SAMD (Table 6). Total metal removal was 8.6 and 4.5 percent with 1.2 and 0.85 percent separated as coadsorbed metal. Approximately 63 percent of the added surfactant remained in the bottoms stream. The error in material balances was typical of SAMD experiments. Separation efficiencies were essentially the same at the two different feed and sparging rates.

An additional experiment in the countercurrent mode was conducted on the fourth day after delivery of the acid drainage. The results (Table 6) are consistent with previous tests except for the abnormally low measured surfactant concentration and surface throughput in the foam. The measured surface throughput of coadsorbed metal also appears to be low. The surfactant balance between feed and bottom

flows indicates that surfactant analysis of the foamate was incorrect due most probably to surfactant loss onto sampling containers at the high VR of 23. As with SAMD, no advantage for operation in the stripping mode compared to the simple mode was found with AMD. SAMD appears to be a valid laboratory substitute for low pH, high Fe(II) AMD, at least for foam separation studies.

SECTION VIII

SURFACTANT REGENERATION

Surfactant represents the principle expense in foam separation of AMD and thus its recovery and reuse in a cyclic pattern would be required for the process to be economically competitive. As a preliminary investigation of surfactant recovery, the addition of base to collapsed foam was tested to determine if surfactant and hydrolyzable metals (Fe, Al and Mn) could be separated by pH increase.

The hydrous oxide of Fe(III) begins to precipitate in weak acidic solution of pH about 4; precipitation is generally complete at or before pH 7. Hydrous aluminum oxide begins to precipitate at pH 3 or higher and is completely precipitated at or before pH 7; at about pH 9 resolution is evident. Thus for initial tests, sufficient base was used to bring the pH up to approximately 7.

Hydrous ferric and aluminum oxides tend to coprecipitate cations at higher pH, which would be desirable in this case. However, excess base would also be a cost factor. Coprecipitation of cationic species can be promoted by rapid addition of base which promotes precipitation in local excess of hydroxide.

Experiments were conducted with the collapsed foam collected from SAMD and AMD experiments. Standardized NaOH was added to filtered and unfiltered foamate samples. The samples (three replicates) were continuously stirred and pH was continuously recorded. Once the precipitate was formed it was allowed to settle briefly before supernatant aliquots were taken for surfactant and metals analysis. Some aliquots were taken up to 3 days after precipitate formation to determine if aging had any effect on supernatant composition. Supernatant samples were either centrifuged or filtered (0.45 μ membrane filter) to remove solids before analysis. Some foamate samples were filtered to determine the amount and nature of solid material.

Tests results for SAMD and AMD, although different in detail, generally agree (Table 8). From 41 to 62 weight percent of the collapsed foam is solid surfactant. Fe, Al and Mn are precipitated to a greater extent than Ca and Mg.

TABLE 8

Recovery of NaDS from Collapsed Foam
by Addition of NaOH

	NaDS	Fe	Ca	Mg (Units; ppm)	Mn	Al	pH
<u>Foam from SAMD</u>							
Collapsed foam	487	209	85	28	8.5	27	2.3
Collapsed foam, filtrate 42 Whatman	286	206	70	25	8.2	25	2.3
Supernatant (1) solution	88	0.75	53	8.3	0.03	0.33	8.0-8.5
Percent removed filtration, 42 Whatman	41	1.4	6.2	9.0	3.5	10	
Percent removed filtration plus precipitation	82	99	38	70	> 99	> 98	
<u>Foam from AMD</u>							
Collapsed foam	510	136	123	35	3.8	46	2.7
Collapsed foam, filtrate 42 Whatman	194	99	99	35	3.8	43	2.7
Collapsed foam, filtrate 0.45 membrane	194	102	99	35	3.8	44	2.7

(1) Supernatant solution from addition of 0.150N NaOH to filtered collapsed foam (42 Whatman)

TABLE 8 (continued)

		NaDS	Fe	Ca	Mg	Mn	Al	pH
		(Units; ppm)						
Supernatant solution, centrifuged replicate	(2)							
	1	265	0.10	72	25	0.92	< 1	7.2
	2	270	0.20	82	27	1.2	< 1	6.9
	3	265	0.15	78	27	1.2	< 1	7.0
Supernatant solution, filtered (0.45) replicate								
	1	265	0.12	75	26	0.85	< 1	7.2
	2	265	< .1	77	27	1.3	< 1	6.9
	3	265	< .1	77	28	1.2	< 1	7.0
Percent removed filtration 42 Whatman		62	27	20	0	0	6	
Percent removed filtration 0.45 membrane		62	25	20	0	0	4	
Percent removed precipitation		48	> 99	37	21	71	> 98	

(2) Supernatant solution from addition of 0.147N NaOH to unfiltered collapsed foam

The solution resulting from base treatment of foamate contains on the average 265 ppm NaDS, less than 2 ppm total Fe, Mn and Al, 77 ppm Ca and 27 ppm Mg. This represents 52 percent recovery of surfactant present in the foamate with the removal of > 99 percent iron, > 98 percent Al and 71 percent Mn.

No noticeable difference in separation occurred between rapid (14 min.) or slow (90 min.) base titration of foamate.

Supernatant pH values tended to drop slightly during the first two hours after which they remained constant. For example, with the AMD foamate samples (Table 8) the pH of the first replicate dropped from 7.2 to 6.3, the second replicate from 6.9 to 6.2 and the third replicate from 7.0 to 6.3 all within two hours; 24 hours later the pH had not changed.

Calculations based on the foamate from the AMD experiments indicate an average of 1.5×10^{-2} moles NaOH are required to precipitate (at pH 7) the metals from a liter of foamate. Titration curves indicate that possibly 9.4×10^{-3} moles NaOH may be sufficient at pH 4-5.

SECTION IX

ECONOMIC EVALUATION AND SUMMARY

The effectiveness of foam separation for the extraction of metals from AMD is low (Figure 10). Approximately 6 percent of the metals are removed per pass under the practical operating limits of the 6 in.-dia. column; of this 6 percent approximately 1 percent is removed as coadsorbed metal, the remainder as interstitial liquid in concentration equal to that in the pool. Minimum surfactant concentration is determined by that required to produce a foam of sufficient persistence to remain intact during protracted drainage which is necessary to reduce foam density and liquid carry-over in the tops. The inherent low foamability of AMD requires a surfactant concentration of about 200 ppm, the majority of which remains in the bottoms.

With surfactant concentration equal to 235 ppm in the supernatant liquid after the surfactant regeneration step, reusable surfactant amounts to 6 percent of that in the feed, dissolved in liquid equal to approximately 5 percent of the feed stream. Loss of surfactant, 74 mole percent to the bottoms and 20 mole percent to the sludge, represents a major technical and economic obstacle to efficient operation.

Chemical and air process costs can be estimated based on the flow scheme presented in Figure 11. A ratio of 1.90 moles surfactant used per mole total metal removed leads to a surfactant cost of 235 dollars per lb-mole metal removed assuming 0.43 dollars per lb surfactant and no surfactant recovery and reuse. This is equivalent to 0.78 dollars per 1000 gal. per foam separation stage which removes approximately 6 mole percent total AMD metals in the ratio 1 mole Fe:0.61 mole Ca:0.32 mole Mg:0.05 mole Mn:0.27 mole Al. To reduce the Fe concentration to 10 ppm, assuming an initial Fe concentration of 200 ppm as in SAMD, would require 19 process stages at a cost of 0.20 dollars per stage per 1000 gal. for each of the first 18 stages plus 0.78 dollars for the last stage giving total cost of 4.50 dollars per 1000 gal. for surfactant. This calculation is based on no surfactant recovery from the overheads but with make-up surfactant added to each successive stage. This calculation assumes no significant reduction in metal extraction rate at reduced metal concentration and thus is only an estimate (Figure 10).

At a sparging air-to-liquid feed volumetric ratio of 16, the cost of air would range between 0.04 and 0.12 dollars per 1000 gal. per stage depending on power costs, or between 0.76 and 2.28 dollars for 19 stages.

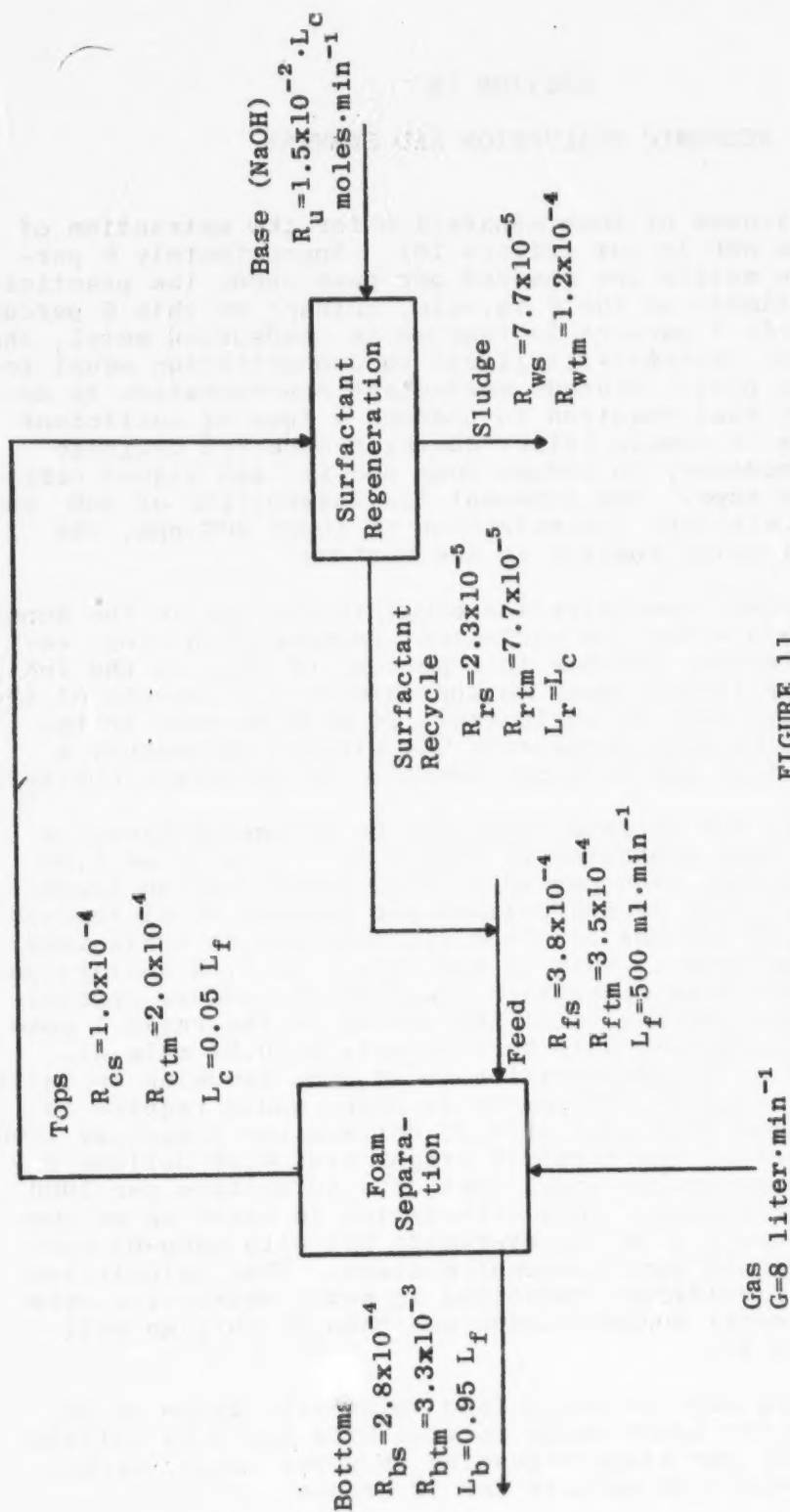


FIGURE 11
 Process Flow Scheme for Foam Separation
 of Metals and Surfactant Regeneration

It is evident from these cost figures that the inherent low extraction capacity of foam fractionation disallows economic feasibility for treatment of waters as concentrated as AMD. Air costs for foaming are comparatively low since the process operates near ambient pressure with little loss. Even so the air costs alone would be prohibitive.

Six mole percent of the total surfactant (23 mole percent of surfactant in the overheads) can be recovered for reuse at a cost of 0.06 dollars per 1000 gal. per stage based on a NaOH cost of 0.25 dollars per lb. This degree of recovery has no economic advantage.

Reduction in surfactant costs may be effected by operation with less surfactant and recovery of a greater percentage of surfactant. This research program investigated the extraction of dissolved metals from AMD by foam separation under conditions which allowed production of persistent foams and protracted foam drainage. Operating with persistent foams requires surfactant concentrations and sparging rates large enough to support a stable foam without surpassing the critical micelle concentration or allowing air velocities high enough to cause foam rupture. At lower surfactant concentrations and sparging rates a transient foam regime is generally produced in which foam drainage and collapse are rapid but controllable. Extraction in a transient foam regime must be lower than for a persistent foam regime due to collapse of surface film and loss of adsorbed material to interstitial liquid followed by drainage back to the pool. Reduction in extraction efficiency could be offset by reduction in surfactant requirements. An optimum sparging rate appears to exist for maximum extraction in a transient foam regime (15); the exact rate being a complex function of chemical and physical parameters must be determined empirically. The maximum occurs at a sparging rate such that the foam drainage rate is significantly greater than the rate of foam collapse (surface loss). This would tend to minimize liquid carryover while maintaining a reasonable metal extraction rate. Such a transient foam system would be characterized by low foam residence times.

A method for surfactant recovery which appears feasible is solvent extraction of surfactant from aqueous solution followed by distillation or spray drying to concentrate surfactant. Such a system has been mentioned (36) but no information on its effectiveness was reported. Surfactant loss to the bottoms flow could be reduced by transient foaming or bubble fractionation, but again air costs would be prohibitive for the treatment of concentrated AMD.

Economic feasibility of foam separation for AMD could be improved with the use of waste air and surfactant. A major source of waste surfactant is sewage, which suggests the waste-plus-waste approach for the synergistic treatment of AMD with alkaline municipal sewage. Studies of the auto-purification of AMD and treated sewage effluent have achieved reductions of 80-95 percent iron, 94-98 percent phosphate, 60-76 percent surfactant, 3-63 percent COD and 70-84 percent acidity in the combined wastes (23)(38). The process consisted of aeration and settling unit operations.

The feasibility of foam separation for sewage treatment has been investigated with the general conclusion that the foamability of sewage is too low since the change from alkyl benzene sulfonate (ABS) to linear alkylate sulfonate (LAS) detergents. Recent research into foam separation of primary and secondary sewage effluents utilizing a combination of foam fractionation and froth flotation has achieved reductions of 70 percent COD, 90 percent phosphate and 40-80 percent suspended solids (27). Air bubbles for particulate flotation and adsorptive extraction were produced by spontaneous degasification of air supersaturated sewage upon pressure release. The best results were achieved with the addition of 300-400 ppm ferric chloride or alum as coagulants; ferrous sulfate was less successful as a coagulant.

These two independent lines of research suggest that if mixtures of AMD and sewage were foamed by degasification, a process which produces fine bubbles capable of maintaining a transient foam in sewage, a significant reduction in COD, phosphate, AMD metals such as Fe and Al, suspended solids, and surfactant could result in addition to neutralization of the wastes. Waste constituents in this type of system are removed non-stoichiometrically with surfactant which tends to reduce treatment costs compared to foam separation of only dissolved, non-surface active constituents of AMD. Preliminary costs for high pressure foaming of sewage along appear promising (27).

SECTION X

ACKNOWLEDGEMENTS

The research program was conducted under the direction of Dr. Peter J. Hason. Construction and operation of the foaming apparatus and analytical work were performed by Messrs. Paul H. Hartman and Jerome H. Jacobs. The report was prepared by Dr. Hanson.

* * *

A significant objective of this project was to investigate practical means of abating mine drainage pollution. Such research projects, intended to assist in the prevention of pollution of water by industry, are required by Section 6 b of the Water Pollution Control Act, as amended. This project of EPA was conducted under the direction of the Pollution Control Analysis Section, Ernst P. Hall, Chief, Dr. James M. Shackelford, Project Manager, and Ronald D. Hill, Project Officer.

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SECTION XII

NOTATIONS AND GLOSSARY

AMD	acid mine drainage
SAMD	synthetic acid mine drainage
CMC	critical micelle concentration
$\bar{d}$	average bubble diameter
FRT	foam residence time, min
L	volumetric liquid rate, $\text{ml} \cdot \text{min}^{-1}$
G	volumetric air sparging rate, $\text{liter} \cdot \text{min}^{-1}$
M	metals in mine drainage, Fe, Ca, Mg, Mn and Al
R	material mass rate, $\text{moles} \cdot \text{min}^{-1}$
S	surfactant
SR	surface material mass rate, $\text{moles} \cdot \text{min}^{-1}$
VR	volume reduction (L_f/L_c)
[]	concentration
Γ	dynamic surface excess, $\text{moles} \cdot \text{cm}^{-2}$
$\Gamma_x/[X]$	distribution ratio, cm

Subscripts

b	refers to liquid pool or bottom flow
c	refers to overhead, foamate or tops flow
f	refers to feed flow
r	refers to recycle of regenerated surfactant
s	refers to surfactant
t	refers to total, e.g., $[M_t]_f$ refers to total metal concentration in the feed flow

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Subscripts

- tm refers to total AMD or SAMD metals, e.g.,
R_{ftm} refers to feed rate of total metal
- u refers to base in surfactant regeneration
- w refers to sludge in surfactant regeneration
- x refers to any variable denoted in text

Adsorption - The concentration of a surface active component of a solution at a phase boundary. In the case of foam separation, the adsorption of surfactant at the gas-liquid interface.

Chelation - An equilibrium reaction between a metal ion and a complexing agent, characterized by formation of multiple bonds between the metal and a molecule of complexing agent and resulting in the formation of a ring structure incorporating the metal ion (see p. 21 and 27).

Coadsorption - The concentration of a surface inactive component of a solution at a phase boundary as a result of its association with a surface active component of the solution. In the case of foam separation, the coadsorption of metal ions with adsorbed surfactant at the gas-liquid interface.

Critical Micelle Concentration - The surfactant concentration at which significant aggregation of surfactant molecules into micelles begins.

Dynamic Surface Excess, Γ - Defined by equation (2), p. 23. The surface excess measured in a flowing foam column (see p. 22-23).

Exchange Capacity - The theoretical maximum time-rate of material removal per unit cross-sectional area of foam column. (See p. 37-39 for discussion and derivation.)

Extraction Rate - The time-rate of adsorbed or coadsorbed material being removed from solution by the foam. (See p. 37-40 and Figure 10. Extraction rate and separation rate used synonymously.)

Foam Coalescence - The rupture of bubble walls resulting in foam collapse and a change from a two phase liquid-gas system to a single liquid phase.

Foam Density - The ratio of the gas-free volume of liquid contained in a foam, to the volume of the original foam.

Micelles - Aggregates of about a hundred monomer surfactant units of roughly spherical shape which form as surfactant concentration is increased. The change from monomeric to polymeric units marks the boundary between true and colloidal solutions.

Surface Excess, Γ_i - Defined by Gibbs model, equation (1), p. 6. The surface excess of solvent is zero. Thus, a solute i with a positive surface excess means that the liquid containing a unit area of surface contains Γ_i more of solute than the volume of bulk liquid which contains the same amount of solvent.

Surfactant - An acronym for "surface active agent". Often characterized by a linear molecular structure which is composed of solvent compatible radicals at one end and solvent incompatible radicals at the other end, these solutes invariably reduce the surface energy of their solvents by collecting at an interface. (See p. 6, 21, and 22 for further discussion of surfactants as they apply to this study.

Synthetic Acid Mine Drainage, SAMD -

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.344 g	} Dissolved in one liter of 0.01 N H_2SO_4
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	0.024 g	
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	0.186 g	
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.997 g	
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.246 g	

1	Accession Number	2	Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
			Ø5D	
5	Organization HORIZONS INCORPORATED, Cleveland, Ohio			
6	Title FOAM SEPARATION OF ACID MINE DRAINAGE			
10	Author(s) Hanson, Peter J.		16	Project Designation EPA Project 14010 FUI, Contract 14-12-876
			21	Note
22	Citation Water Pollution Control Research Series, 14010 FUI 10/71 Environmental Protection Agency, Washington, D. C.			
23	Descriptors (Starred First) * Acid Mine Drainage, * Foam Separation, * Mine Drainage Treatment, * Surfactants, * Iron, * Economics, Metal Cations, Surfactant Regeneration			
25	Identifiers (Starred First)			

27 Abstract Laboratory studies of continuous flow foam separation in a persistent foam regime were conducted to determine the optimum operating conditions for maximum extraction of dissolved metal cations (Fe, Ca, Mg, Mn and Al) from acid mine drainage. Foaming experiments were conducted in a 6 in.-diameter glass column capable of liquid flow rates of 3-12 gal. per hour. The effects of pH, chelate addition, surfactant type and concentration, air sparging rate, metal concentration and foam drainage were investigated in relation to metal extraction.

The average extraction rate obtained was 1.9×10^{-7} moles total metal per cm^2 column cross-section area per minute which is approximately 4.0×10^{-7} equivalents per cm^2 per minute. Operation in simple and countercurrent foaming modes produced similar extraction rates for acid mine drainage.

The low extraction capacity of foam fractionation renders the process economically unfeasible for the treatment of acid mine drainage. The principal chemical cost is for surfactant followed by air.

Surfactant regeneration from foam by addition of base was investigated for surfactant reuse and cost reduction. (Hanson-Horizons)

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